Waste Isolation Pilot Plant

Compliance Certification Application

Reference 234a

EPA (U.S. Environmental Protection Agency). 1986.
Test Methods for Evaluating Solid Waste, Physical/Chemical Methods, SW-846, 3rd ed., Office of Solid Waste and Emergency Response, Washington, D.C. Volume IA.

Submitted in accordance with 40 CFR §194.13, Submission of Reference Materials.

United States
Environmental Protection
Agency

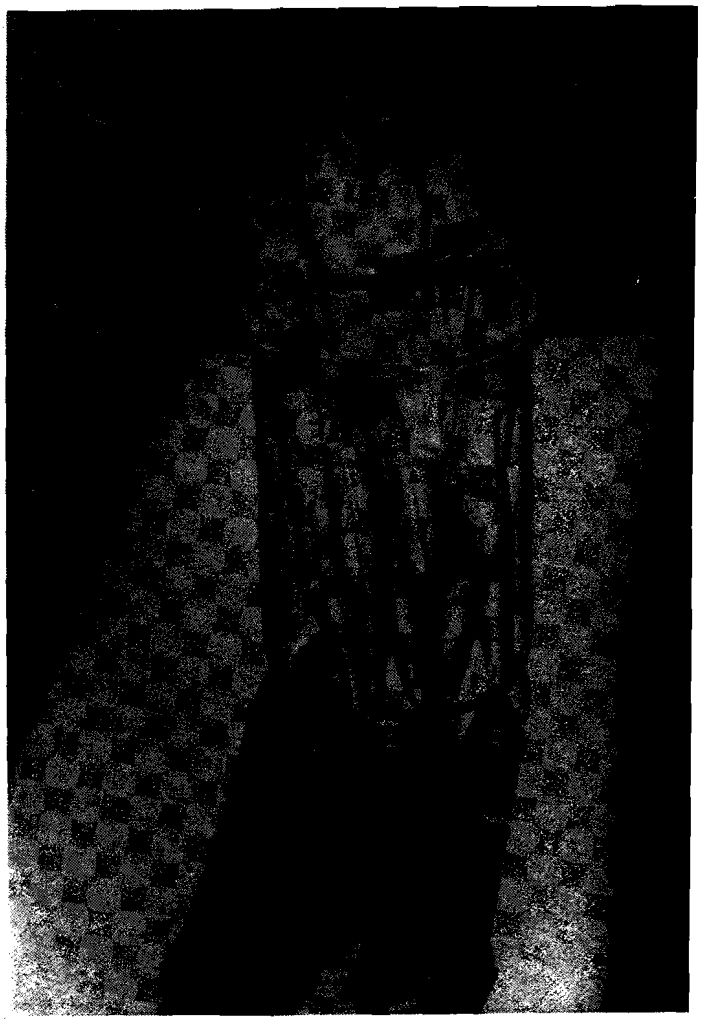
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Solid Waste

Test Methods for Evaluating Solid Waste

Volume IA: Laboratory Manual Physical/Chemical Methods



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DISCLAIMER

Mention of trade names or commercial products does not constitute endorsement or recommendation for use by the U.S. Environmental Protection Agency.

SW-846 methods are designed to be used with equipment from any manufacturer that results in suitable method performance (as assessed by accuracy, precision, detection limits and matrix compatibility). In several SW-846 methods, equipment specifications and settings are given for the specific instrument used during method development, or subsequently approved for use in the method. These references are made to provide the best possible guidance to laboratories using this manual. Equipment not specified in the method may be used as long as the laboratory achieves equivalent or superior method performance. If alternate equipment is used, the laboratory must follow the manufacturer's instructions for their particular instrument.

Since many types and sizes of glassware and supplies are commercially available, and since it is possible to prepare reagents and standards in many different ways, those specified in these methods may be replaced by any similar types as long as this substitution does not affect the overall quality of the analyses.

ABSTRACT

Test Methods for Evaluating Solid Waste, Physical/Chemical Methods (SW-846) provides test procedures and guidance which are recommended for use in conducting the evaluations and measurements needed to comply with the Resource Conservation and Recovery Act (RCRA), Public Law 94-580. These methods are approved by the U.S. Environmental Protection Agency for obtaining data to satisfy the requirements of 40 CFR Parts 122 through 270. This manual presents the state-of-the-art in routine analytical testing adapted for the RCRA program. It contains procedures for field and laboratory quality control, sampling, determining hazardous constituents in wastes, determining the hazardous characteristics of wastes (toxicity, ignitability, reactivity, and corrosivity), and for determining physical properties of wastes. It also contains guidance on how to select appropriate methods.

Several of the hazardous waste regulations under Subtitle C of RCRA require that specific testing methods described in SW-846 be employed for certain applications. Refer to 40 *Code of Federal Regulations* (CFR), Parts 260 through 270, for those specific requirements. Any reliable analytical method may be used to meet other requirements under Subtitle C of RCRA.

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NOTE: A suffix of "A" in the method number indicates revision one (the method has been revised once). A suffix of "B" in the method number indicates revision two (the method has been revised twice). A suffix of "C" in the method number indicates revision three (the method has been revised three times). **In order to properly document the method used for analysis, the entire method number including the suffix letter designation (e.g., A, B, or C) must be identified by the analyst.** A method reference found within the RCRA regulations and the text of SW-846 methods and chapters refers to the latest promulgated revision of the method, even though the method number does not include the appropriate letter suffix.

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METHOD STATUS TABLE
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March 1995

- Use this table as a reference guide to identify the promulgation status of SW-846 methods.
- The methods in this table are listed sequentially by number.
- This table should not be used as a Table of Contents for SW-846. Refer to the Table of Contents found in Final Update IIB (dated January 1995) for the order in which the methods appear in SW-846.

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METH NO. THIRD ED DATED 9/86	METH NO. FINAL UPDATE I DATED 7/92	METH NO. FIN. UP. II (9/94), IIA (8/93), & IIB (1/95)	METHOD TITLE	SW-846 VOLUME/ CHAPTER/ SECTION LOCATION	CURRENT PROMUL-GATED METHOD
0010	--	--	Modified Method 5 Sampling Train	Vol II Chap 10	0010 Rev 0 9/86
0020	--	--	Source Assessment Sampling System (SASS)	Vol II Chap 10	0020 Rev 0 9/86
0030	--	--	Volatile Organic Sampling Train	Vol II Chap 10	0030 Rev 0 9/86
1010	--	--	Pensky-Martens Closed-Cup Method for Determining Ignitability	Vol IC Chap 8 Sec 8.1	1010 Rev 0 9/86
1020	1020A	--	Setaflash Closed-Cup Method for Determining Ignitability	Vol IC Chap 8 Sec 8.1	1020A Rev 1 7/92
1110	--	--	Corrosivity Toward Steel	Vol IC Chap 8 Sec 8.2	1110 Rev 0 9/86
1310	1310A	--	Extraction Procedure (EP) Toxicity Test Method and Structural Integrity Test	Vol IC Chap 8 Sec 8.4	1310A Rev 1 7/92
--	1311	--	Toxicity Characteristic Leaching Procedure	Vol IC Chap 8 Sec 8.4	1311 Rev 0 7/92

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--	--	1312 (Up. II)	Synthetic Precipitation Leaching Procedure	Vol IC Chap 6	1312 Rev 0 9/94
1320	--	--	Multiple Extraction Procedure	Vol IC Chap. 6	1320 Rev 0 9/86
1330	1330A	--	Extraction Procedure for Oily Wastes	Vol IC Chap 6	1330A Rev 1 7/92
3005	3005A	--	Acid Digestion of Waters for Total Recoverable or Dissolved Metals for Analysis by FLAA or ICP Spectroscopy	Vol IA Chap 3 Sec 3.2	3005A Rev 1 7/92
3010	3010A	--	Acid Digestion of Aqueous Samples and Extracts for Total Metals for Analysis by FLAA or ICP Spectroscopy	Vol IA Chap 3 Sec 3.2	3010A Rev 1 7/92
--	--	3015 (Up. II)	Microwave Assisted Acid Digestion of Aqueous Samples and Extracts	Vol IA Chap 3 Sec 3.2	3015 Rev 0 9/94
3020	3020A	--	Acid Digestion of Aqueous Samples and Extracts for Total Metals for Analysis by GFAA Spectroscopy	Vol IA Chap 3 Sec 3.2	3020A Rev 1 7/92

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3040	--	--	Dissolution Procedure for Oils, Greases, or Waxes	Vol IA Chap 3 Sec 3.2	3040 Rev 0 9/86
3050	3050A	--	Acid Digestion of Sediments, Sludges, and Soils	Vol IA Chap 3 Sec 3.2	3050A Rev 1 7/92
--	--	3051 (Up. II)	Microwave Assisted Acid Digestion of Sediments, Sludges, Soils, and Oils	Vol IA Chap 3 Sec 3.2	3051 Rev 0 9/94
3500	3500A	--	Organic Extraction and Sample Preparation	Vol IB Chap 4 Sec 4.2.1	3500A Rev 1 7/92
3510	3510A	3510B (Up. II)	Separatory Funnel Liquid-Liquid Extraction	Vol IB Chap 4 Sec 4.2.1	3510B Rev 2 9/94
3520	3520A	3520B (Up. II)	Continuous Liquid-Liquid Extraction	Vol IB Chap 4 Sec 4.2.1	3520B Rev 2 9/94
3540	3540A	3540B (Up. II)	Soxhlet Extraction	Vol IB Chap 4 Sec 4.2.1	3540B Rev 2 9/94
--	--	3541 (Up. II)	Automated Soxhlet Extraction	Vol IB Chap 4 Sec 4.2.1	3541 Rev 0 9/94
3550	--	3550A (Up. II)	Ultrasonic Extraction	Vol IB Chap 4 Sec 4.2.1	3550A Rev 1 9/94

SW-846 METHOD STATUS TABLE (3/95), CONTINUED

METH NO. THIRD ED DATED 9/86	METH NO. FINAL UPDATE I DATED 7/92	METH NO. FIN. UP. II (9/94), IIA (8/93), & IIB (1/95)	METHOD TITLE	SW-846 VOLUME/ CHAPTER/ SECTION LOCATION	CURRENT PROMUL-GATED METHOD
3580	3580A	--	Waste Dilution	Vol IB Chap 4 Sec 4.2.1	3580A Rev 1 7/92
3600	3600A	3600B (Up. II)	Cleanup	Vol IB Chap 4 Sec 4.2.2	3600B Rev 2 9/94
3610	3610A	--	Alumina Column Cleanup	Vol IB Chap 4 Sec 4.2.2	3610A Rev 1 7/92
3611	3611A	--	Alumina Column Cleanup and Separation of Petroleum Wastes	Vol IB Chap 4 Sec 4.2.2	3611A Rev 1 7/92
3620	3620A	--	Florisil Column Cleanup	Vol IB Chap 4 Sec 4.2.2	3620A Rev 1 7/92
3630	3630A	3630B (Up. II)	Silica Gel Cleanup	Vol IB Chap 4 Sec 4.2.2	3630B Rev 2 9/94
3640	--	3640A (Up. II)	Gel-Permeation Cleanup	Vol IB Chap 4 Sec 4.2.2	3640A Rev 1 9/94
3650	3650A	--	Acid-Base Partition Cleanup	Vol IB Chap 4 Sec 4.2.2	3650A Rev 1 7/92
3660	3660A	--	Sulfur Cleanup	Vol IB Chap 4 Sec 4.2.2	3660A Rev 1 7/92

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--	--	3665 (Up. II)	Sulfuric Acid/Permanganate Cleanup	Vol IB Chap 4 Sec 4.2.2	3665 Rev 0 9/94
3810	--	--	Headspace	Vol IB Chap 4 Sec 4.4	3810 Rev 0 9/86
3820	--	--	Hexadecane Extraction and Screening of Purgeable Organics	Vol IB Chap 4 Sec 4.4	3820 Rev 0 9/86
--	--	4010 (Up. IIA)	Screening for Pentachlorophenol by Immunoassay	Vol IB Chap 4 Sec 4.4	4010 Rev 0 8/93
5030	5030A	--	Purge-and-Trap	Vol IB Chap 4 Sec 4.2.1	5030A Rev 1 7/92
5040	--	5040A (Up. II)	Analysis of Sorbent Cartridges from Volatile Organic Sampling Train (VOST): Gas Chromatography/ Mass Spectrometry Technique	Vol IB Chap 4 Sec 4.2.1	5040A Rev 1 9/94
--	--	5041 (Up. II)	Protocol for Analysis of Sorbent Cartridges from Volatile Organic Sampling Train (VOST): Wide-bore Capillary Column Technique	Vol IB Chap 4 Sec 4.2.1	5041 Rev 0 9/94

SW-846 METHOD STATUS TABLE (3/95), CONTINUED

METH NO. THIRD ED DATED 9/86	METH NO. FINAL UPDATE I DATED 7/92	METH NO. FIN. UP. II (9/94), IIA (8/93), & IIB (1/95)	METHOD TITLE	SW-846 VOLUME/ CHAPTER/ SECTION LOCATION	CURRENT PROMUL-GATED METHOD
--	--	5050 (Up. II)	Bomb Preparation Method for Solid Waste	Vol IC Chap 5	5050 Rev 0 9/94
6010	6010A	--	Inductively Coupled Plasma - Atomic Emission Spectroscopy	Vol IA Chap 3 Sec 3.3	6010A Rev 1 7/92
--	--	6020 (Up. II)	Inductively Coupled Plasma - Mass Spectrometry	Vol IA Chap 3 Sec 3.3	6020 Rev 0 9/94
7000	7000A	--	Atomic Absorption Methods	Vol IA Chap 3 Sec 3.3	7000A Rev 1 7/92
7020	--	--	Aluminum (Atomic Absorption, Direct Aspiration)	Vol IA Chap 3 Sec 3.3	7020 Rev 0 9/86
7040	--	--	Antimony (Atomic Absorption, Direct Aspiration)	Vol IA Chap 3 Sec 3.3	7040 Rev 0 9/86
7041	--	--	Antimony (Atomic Absorption, Furnace Technique)	Vol IA Chap 3 Sec 3.3	7041 Rev 0 9/86
7060	--	7060A (Up. II)	Arsenic (Atomic Absorption, Furnace Technique)	Vol IA Chap 3 Sec 3.3	7060A Rev 1 9/94
7061	7061A	--	Arsenic (Atomic Absorption, Gaseous Hydride)	Vol IA Chap 3 Sec 3.3	7061A Rev 1 7/92

SW-846 METHOD STATUS TABLE (3/95), CONTINUED

METH NO. THIRD ED DATED 9/86	METH NO. FINAL UPDATE I DATED 7/92	METH NO. FIN. UP. II (9/94), IIA (8/93), & IIB (1/95)	METHOD TITLE	SW-846 VOLUME/ CHAPTER/ SECTION LOCATION	CURRENT PROMUL-GATED METHOD
--	--	7062 (Up. II)	Antimony and Arsenic (Atomic Absorption, Borohydride Reduction)	Vol IA Chap 3 Sec 3.3	7062 Rev 0 9/94
7080	--	7080A (Up. II)	Barium (Atomic Absorption, Direct Aspiration)	Vol IA Chap 3 Sec 3.3	7080A Rev 1 9/94
--	7081	--	Barium (Atomic Absorption, Furnace Technique)	Vol IA Chap 3 Sec 3.3	7081 Rev 0 7/92
7090	--	--	Beryllium (Atomic Absorption, Direct Aspiration)	Vol IA Chap 3 Sec 3.3	7090 Rev 0 9/86
7091	--	--	Beryllium (Atomic Absorption, Furnace Technique)	Vol IA Chap 3 Sec 3.3	7091 Rev 0 9/86
7130	--	--	Cadmium (Atomic Absorption, Direct Aspiration)	Vol IA Chap 3 Sec 3.3	7130 Rev 0 9/86
7131	--	7131A (Up. II)	Cadmium (Atomic Absorption, Furnace Technique)	Vol IA Chap 3 Sec 3.3	7131A Rev 1 9/94
7140	--	--	Calcium (Atomic Absorption, Direct Aspiration)	Vol IA Chap 3 Sec 3.3	7140 Rev 0 9/86
7190	--	--	Chromium (Atomic Absorption, Direct Aspiration)	Vol IA Chap 3 Sec 3.3	7190 Rev 0 9/86

SW-846 METHOD STATUS TABLE (3/95), CONTINUED

METH NO. THIRD ED DATED 9/86	METH NO. FINAL UPDATE I DATED 7/92	METH NO. FIN. UP. II (9/94), IIA (8/93), & IIB (1/95)	METHOD TITLE	SW-846 VOLUME/ CHAPTER/ SECTION LOCATION	CURRENT PROMUL-GATED METHOD
7191	--	--	Chromium (Atomic Absorption, Furnace Technique)	Vol IA Chap 3 Sec 3.3	7191 Rev 0 9/86
7195	--	--	Chromium, Hexavalent (Coprecipitation)	Vol IA Chap 3 Sec 3.3	7195 Rev 0 9/86
7196	7196A	--	Chromium, Hexavalent (Colorimetric)	Vol IA Chap 3 Sec 3.3	7196A Rev 1 7/92
7197	--	--	Chromium, Hexavalent (Chelation/ Extraction)	Vol IA Chap 3 Sec 3.3	7197 Rev 0 9/86
7198	--	--	Chromium, Hexa-valent (Differ-ential Pulse Polarography)	Vol IA Chap 3 Sec 3.3	7198 Rev 0 9/86
7200	--	--	Cobalt (Atomic Absorption, Direct Aspiration)	Vol IA Chap 3 Sec 3.3	7200 Rev 0 9/86
7201	--	--	Cobalt (Atomic Absorption, Furnace Technique)	Vol IA Chap 3 Sec 3.3	7201 Rev 0 9/86
7210	--	--	Copper (Atomic Absorption, Direct Aspiration)	Vol IA Chap 3 Sec 3.3	7210 Rev 0 9/86
--	7211	--	Copper (Atomic Absorption, Furnace Technique)	Vol IA Chap 3 Sec 3.3	7211 Rev 0 7/92

SW-846 METHOD STATUS TABLE (3/95), CONTINUED

METH NO. THIRD ED DATED 9/86	METH NO. FINAL UPDATE I DATED 7/92	METH NO. FIN. UP. II (9/94), IIA (8/93), & IIB (1/95)	METHOD TITLE	SW-846 VOLUME/ CHAPTER/ SECTION LOCATION	CURRENT PROMUL-GATED METHOD
7380	--	--	Iron (Atomic Absorption, Direct Aspiration)	Vol IA Chap 3 Sec 3.3	7380 Rev 0 9/86
--	7381	--	Iron (Atomic Absorption, Furnace Technique)	Vol IA Chap 3 Sec 3.3	7381 Rev 0 7/92
7420	--	--	Lead (Atomic Absorption, Direct Aspiration)	Vol IA Chap 3 Sec 3.3	7420 Rev 0 9/86
7421	--	--	Lead (Atomic Absorption, Furnace Technique)	Vol IA Chap 3 Sec 3.3	7421 Rev 0 9/86
--	7430	--	Lithium (Atomic Absorption, Direct Aspiration)	Vol IA Chap 3 Sec 3.3	7430 Rev 0 7/92
7450	--	--	Magnesium (Atomic Absorption, Direct Aspiration)	Vol IA Chap 3 Sec 3.3	7450 Rev 0 9/86
7460	--	--	Manganese (Atomic Absorption, Direct Aspiration)	Vol IA Chap 3 Sec 3.3	7460 Rev 0 9/86
--	7461	--	Manganese (Atomic Absorption, Furnace Technique)	Vol IA Chap 3 Sec 3.3	7461 Rev 0 7/92
7470	--	7470A (Up. II)	Mercury in Liquid Waste (Manual Cold-Vapor Technique)	Vol IA Chap 3 Sec 3.3	7470A Rev 1 9/94

SW-846 METHOD STATUS TABLE (3/95), CONTINUED

METH NO. THIRD ED DATED 9/86	METH NO. FINAL UPDATE I DATED 7/92	METH NO. FIN. UP. II (9/94), IIA (8/93), & IIB (1/95)	METHOD TITLE	SW-846 VOLUME/ CHAPTER/ SECTION LOCATION	CURRENT PROMUL-GATED METHOD
7471	--	7471A (Up. II)	Mercury in Solid or Semisolid Waste (Manual Cold-Vapor Technique)	Vol IA Chap 3 Sec 3.3	7471A Rev 1 9/94
7480	--	--	Molybdenum (Atomic Absorption, Direct Aspiration)	Vol IA Chap 3 Sec 3.3	7480 Rev 0 9/86
7481	--	--	Molybdenum (Atomic Absorption, Furnace Technique)	Vol IA Chap 3 Sec 3.3	7481 Rev 0 9/86
7520	--	--	Nickel (Atomic Absorption, Direct Aspiration)	Vol IA Chap 3 Sec 3.3	7520 Rev 0 9/86
7550	--	--	Osmium (Atomic Absorption, Direct Aspiration)	Vol IA Chap 3 Sec 3.3	7550 Rev 0 9/86
7610	--	--	Potassium (Atomic Absorption, Direct Aspiration)	Vol IA Chap 3 Sec 3.3	7610 Rev 0 9/86
7740	--	--	Selenium (Atomic Absorption, Furnace Technique)	Vol IA Chap 3 Sec 3.3	7740 Rev 0 9/86
7741	--	7741A (Up. II)	Selenium (Atomic Absorption, Gaseous Hydride)	Vol IA Chap 3 Sec 3.3	7741A Rev 1 9/94

SW-846 METHOD STATUS TABLE (3/95), CONTINUED

METH NO. THIRD ED DATED 9/86	METH NO. FINAL UPDATE I DATED 7/92	METH NO. FIN. UP. II (9/94), IIA (8/93), & IIB (1/95)	METHOD TITLE	SW-846 VOLUME/ CHAPTER/ SECTION LOCATION	CURRENT PROMUL-GATED METHOD
--	--	7742 (Up. II)	Selenium (Atomic Absorption, Borohydride Reduction)	Vol IA Chap 3 Sec 3.3	7742 Rev 0 9/94
7760	7760A	--	Silver (Atomic Absorption, Direct Aspiration)	Vol IA Chap 3 Sec 3.3	7760A Rev 1 7/92
--	7761	--	Silver (Atomic Absorption, Furnace Technique)	Vol IA Chap 3 Sec 3.3	7761 Rev 0 7/92
7770	--	--	Sodium (Atomic Absorption, Direct Aspiration)	Vol IA Chap 3 Sec 3.3	7770 Rev 0 9/86
--	7780	--	Strontium (Atomic Absorption, Direct Aspiration)	Vol IA Chap 3 Sec 3.3	7780 Rev 0 7/92
7840	--	--	Thallium (Atomic Absorption, Direct Aspiration)	Vol IA Chap 3 Sec 3.3	7840 Rev 0 9/86
7841	--	--	Thallium (Atomic Absorption, Furnace Technique)	Vol IA Chap 3 Sec 3.3	7841 Rev 0 9/86
7870	--	--	Tin (Atomic Absorption, Direct Aspiration)	Vol IA Chap 3 Sec 3.3	7870 Rev 0 9/86
7910	--	--	Vanadium (Atomic Absorption, Direct Aspiration)	Vol IA Chap 3 Sec 3.3	7910 Rev 0 9/86

SW-846 METHOD STATUS TABLE (3/95), CONTINUED

METH NO. THIRD ED DATED 9/86	METH NO. FINAL UPDATE I DATED 7/92	METH NO. FIN. UP. II (9/94), IIA (8/93), & IIB (1/95)	METHOD TITLE	SW-846 VOLUME/ CHAPTER/ SECTION LOCATION	CURRENT PROMUL-GATED METHOD
7911	--	--	Vanadium (Atomic Absorption, Furnace Technique)	Vol IA Chap 3 Sec 3.3	7911 Rev 0 9/86
7950	--	--	Zinc (Atomic Absorption, Direct Aspiration)	Vol IA Chap 3 Sec 3.3	7950 Rev 0 9/86
--	7951	--	Zinc (Atomic Absorption, Furnace Technique)	Vol IA Chap 3 Sec 3.3	7951 Rev 0 7/92
8000	8000A	--	Gas Chromatography	Vol IB Chap 4 Sec 4.3.1	8000A Rev 1 7/92
8010	8010A	8010B (Up. II)	Halogenated Volatile Organics by Gas Chromatography	Vol IB Chap 4 Sec 4.3.1	8010B Rev 2 9/94
--	8011	--	1,2-Dibromoethane and 1,2-Dibromo-3-chloropropane by Microextraction and Gas Chromatography	Vol IB Chap 4 Sec 4.3.1	8011 Rev 0 7/92
8015	8015A	--	Nonhalogenated Volatile Organics by Gas Chromatography	Vol IB Chap 4 Sec 4.3.1	8015A Rev 1 7/92
8020	--	8020A (Up. II)	Aromatic Volatile Organics by Gas Chromatography	Vol IB Chap 4 Sec 4.3.1	8020A Rev 1 9/94

SW-846 METHOD STATUS TABLE (3/95), CONTINUED

METH NO. THIRD ED DATED 9/86	METH NO. FINAL UPDATE I DATED 7/92	METH NO. FIN. UP. II (9/94), IIA (8/93), & IIB (1/95)	METHOD TITLE	SW-846 VOLUME/ CHAPTER/ SECTION LOCATION	CURRENT PROMUL-GATED METHOD
--	8021	8021A (Up. II)	Halogenated Volatiles by Gas Chromatography Using Photoionization and Electrolytic Conductivity Detectors in Series: Capillary Column Technique	Vol IB Chap 4 Sec 4.3.1	8021A Rev 1 9/94
8030	8030A	--	Acrolein and Acrylonitrile by Gas Chromatography	Vol IB Chap 4 Sec 4.3.1	8030A Rev 1 7/92
--	--	8031 (Up. II)	Acrylonitrile by Gas Chromatography	Vol IB Chap 4 Sec 4.3.1	8031 Rev 0 9/94
--	--	8032 (Up. II)	Acrylamide by Gas Chromatography	Vol IB Chap 4 Sec 4.3.1	8032 Rev 0 9/94
8040	8040A	--	Phenols by Gas Chromatography	Vol IB Chap 4 Sec 4.3.1	8040A Rev 1 7/92
8060	--	--	Phthalate Esters	Vol IB Chap 4 Sec 4.3.1	8060 Rev 0 9/86
--	--	8061 (Up. II)	Phthalate Esters by Capillary Gas Chromatography with Electron Capture Detection (GC/ECD)	Vol IB Chap 4 Sec 4.3.1	8061 Rev 0 9/94

SW-846 METHOD STATUS TABLE (3/95), CONTINUED

METH NO. THIRD ED DATED 9/86	METH NO. FINAL UPDATE I DATED 7/92	METH NO. FIN. UP. II (9/94), IIA (8/93), & IIB (1/95)	METHOD TITLE	SW-846 VOLUME/ CHAPTER/ SECTION LOCATION	CURRENT PROMUL-GATED METHOD
--	8070	--	Nitrosamines by Gas Chromatography	Vol IB Chap 4 Sec 4.3.1	8070 Rev 0 7/92
8080	--	8080A (Up. II)	Organochlorine Pesticides and Polychlorinated Biphenyls by Gas Chromatography	Vol IB Chap 4 Sec 4.3.1	8080A Rev 1 9/94
--	--	8081 (Up. II)	Organochlorine Pesticides and PCBs as Aroclors by Gas Chromatography: Capillary Column Technique	Vol IB Chap 4 Sec 4.3.1	8081 Rev 0 9/94
8090	--	--	Nitroaromatics and Cyclic Ketones	Vol IB Chap 4 Sec 4.3.1	8090 Rev 0 9/86
8100	--	--	Polynuclear Aromatic Hydrocarbons	Vol IB Chap 4 Sec 4.3.1	8100 Rev 0 9/86
--	8110	--	Haloethers by Gas Chromatography	Vol IB Chap 4 Sec 4.3.1	8110 Rev 0 7/92
8120	--	8120A (Up. II)	Chlorinated Hydrocarbons by Gas Chromatography	Vol IB Chap 4 Sec 4.3.1	8120A Rev 1 9/94
--	--	8121 (Up. II)	Chlorinated Hydrocarbons by Gas Chromatography: Capillary Column Technique	Vol IB Chap 4 Sec 4.3.1	8121 Rev 0 9/94

SW-846 METHOD STATUS TABLE (3/95), CONTINUED

METH NO. THIRD ED DATED 9/86	METH NO. FINAL UPDATE I DATED 7/92	METH NO. FIN. UP. II (9/94), IIA (8/93), & IIB (1/95)	METHOD TITLE	SW-846 VOLUME/ CHAPTER/ SECTION LOCATION	CURRENT PROMUL-GATED METHOD
8140	--	--	Organophosphorus Pesticides	Vol IB Chap 4 Sec 4.3.1	8140 Rev 0 9/86
--	8141	8141A (Up. II)	Organophosphorus Compounds by Gas Chromatography: Capillary Column Technique	Vol IB Chap 4 Sec 4.3.1	8141A Rev 1 9/94
8150	8150A	8150B (Up. II)	Chlorinated Herbicides by Gas Chromatography	Vol IB Chap 4 Sec 4.3.1	8150B Rev 2 9/94
--	--	8151 (Up. II)	Chlorinated Herbicides by GC Using Methylation or Pentafluoro-benzylation Derivatization: Capillary Column Technique	Vol IB Chap 4 Sec 4.3.1	8151 Rev 0 9/94
8240	8240A	8240B (Up. II)	Volatile Organic Compounds by Gas Chromatography/ Mass Spectrometry (GC/MS)	Vol IB Chap 4 Sec 4.3.2	8240B Rev 2 9/94
8250	--	8250A (Up. II)	Semivolatile Organic Compounds by Gas Chromatog-raphy/Mass Spec-trometry (GC/MS)	Vol IB Chap 4 Sec 4.3.2	8250A Rev 1 9/94
--	8260	8260A (Up. II)	Volatile Organic Compounds by Gas Chromatography/ Mass Spectrometry (GC/MS): Capillary Column Technique	Vol IB Chap 4 Sec 4.3.2	8260A Rev 1 9/94

SW-846 METHOD STATUS TABLE (3/95), CONTINUED

METH NO. THIRD ED DATED 9/86	METH NO. FINAL UPDATE I DATED 7/92	METH NO. FIN. UP. II (9/94), IIA (8/93), & IIB (1/95)	METHOD TITLE	SW-846 VOLUME/ CHAPTER/ SECTION LOCATION	CURRENT PROMUL-GATED METHOD
8270	8270A	8270B (Up. II)	Semivolatile Organic Compounds by Gas Chromatography/Mass Spectrometry (GC/MS): Capillary Column Technique	Vol IB Chap 4 Sec 4.3.2	8270B Rev 2 9/94
--	--	8275 (Up. II)	Thermal Chromatography/Mass Spectrometry (TC/MS) for Screening Semivolatile Organic Compounds	Vol IB Chap 4 Sec 4.4	8275 Rev 0 9/94
8280	--	--	The Analysis of Polychlorinated Dibenzo-p-Dioxins and Polychlorinated Dibenzofurans	Vol IB Chap 4 Sec 4.3.2	8280 Rev 0 9/86
--	--	8290 (Up. II)	Polychlorinated Dibenzodioxins (PCDDs) and Polychlorinated Dibenzofurans (PCDFs) by High-Resolution Gas Chromatography/ High-Resolution Mass Spectrometry (HRGC/HRMS)	Vol IB Chap 4 Sec 4.3.2	8290 Rev 0 9/94
8310	--	--	Polynuclear Aromatic Hydrocarbons	Vol IB Chap 4 Sec 4.3.3	8310 Rev 0 9/86

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METH NO. THIRD ED DATED 9/86	METH NO. FINAL UPDATE I DATED 7/92	METH NO. FIN. UP. II (9/94), IIA (8/93), & IIB (1/95)	METHOD TITLE	SW-846 VOLUME/ CHAPTER/ SECTION LOCATION	CURRENT PROMUL-GATED METHOD
--	--	8315 (Up. II)	Determination of Carbonyl Compounds by High Performance Liquid Chromatography (HPLC)	Vol IB Chap 4 Sec 4.3.3	8315 Rev 0 9/94
--	--	8316 (Up. II)	Acrylamide, Acrylonitrile and Acrolein by High Performance Liquid Chromatography (HPLC)	Vol IB Chap 4 Sec 4.3.3	8316 Rev 0 9/94
--	--	8318 (Up. II)	N-Methylcarbamates by High Performance Liquid Chromatography (HPLC)	Vol IB Chap 4 Sec 4.3.3	8318 Rev 0 9/94
--	--	8321 (Up. II)	Solvent Extractable Non-Volatile Compounds by High Performance Liquid Chromatography/Thermospray/Mass Spectrometry (HPLC/TSP/MS) or Ultraviolet (UV) Detection	Vol IB Chap 4 Sec 4.3.3	8321 Rev 0 9/94
--	--	8330 (Up. II)	Nitroaromatics and Nitramines by High Performance Liquid Chromatography (HPLC)	Vol IB Chap 4 Sec 4.3.3	8330 Rev 0 9/94
--	--	8331 (Up. II)	Tetrazene by Reverse Phase High Performance Liquid Chromatography (HPLC)	Vol IB Chap 4 Sec 4.3.3	8331 Rev 0 9/94

SW-846 METHOD STATUS TABLE (3/95), CONTINUED

METH NO. THIRD ED DATED 9/86	METH NO. FINAL UPDATE I DATED 7/92	METH NO. FIN. UP. II (9/94), IIA (8/93), & IIB (1/95)	METHOD TITLE	SW-846 VOLUME/ CHAPTER/ SECTION LOCATION	CURRENT PROMUL-GATED METHOD
--	--	8410 (Up. II)	Gas Chromatography/Fourier Transform Infrared (GC/FT-IR) Spectrometry for Semivolatile Organics: Capillary Column	Vol IB Chap 4 Sec 4.3.4	8410 Rev 0 9/94
9010	9010A	--	Total and Amenable Cyanide (Colorimetric, Manual)	Vol IC Chap 5	9010A Rev 1 7/92
9012	--	--	Total and Amenable Cyanide (Colorimetric, Automated UV)	Vol IC Chap 5	9012 Rev 0 9/86
--	9013	--	Cyanide Extraction Procedure for Solids and Oils	Vol IC Chap 5	9013 Rev 0 7/92
9020	9020A	9020B (Up. II)	Total Organic Halides (TOX)	Vol IC Chap 5	9020B Rev 2 9/94
--	9021	--	Purgeable Organic Halides (POX)	Vol IC Chap 5	9021 Rev 0 7/92
9022	--	--	Total Organic Halides (TOX) by Neutron Activation Analysis	Vol IC Chap 5	9022 Rev 0 9/86
9030	9030A	--	Acid-Soluble and Acid-Insoluble Sulfides	Vol IC Chap 5	9030A Rev 1 7/92

SW-846 METHOD STATUS TABLE (3/95), CONTINUED

METH NO. THIRD ED DATED 9/86	METH NO. FINAL UPDATE I DATED 7/92	METH NO. FIN. UP. II (9/94), IIA (8/93), & IIB (1/95)	METHOD TITLE	SW-846 VOLUME/ CHAPTER/ SECTION LOCATION	CURRENT PROMUL-GATED METHOD
--	9031	--	Extractable Sulfides	Vol IC Chap 5	9031 Rev 0 7/92
9035	--	--	Sulfate (Colorimetric, Automated, Chloranilate)	Vol IC Chap 5	9035 Rev 0 9/86
9036	--	--	Sulfate (Colori-metric, Auto-mated, Methylthy-mol Blue, AA II)	Vol IC Chap 5	9036 Rev 0 9/86
9038	--	--	Sulfate (Turbidimetric)	Vol IC Chap 5	9038 Rev 0 9/86
9040	--	9040A (Up. II) 9040B (Up. IIB)	pH Electrometric Measurement	Vol IC Chap 6	9040B Rev 2 1/95
9041	9041A	--	pH Paper Method	Vol IC Chap 6	9041A Rev 1 7/92
9045	9045A	9045B (Up. II) 9045C (Up. IIB)	Soil and Waste pH	Vol IC Chap 6	9045C Rev 3 1/95
9050	--	--	Specific Conductance	Vol IC Chap 6	9050 Rev 0 9/86
--	--	9056 (Up. II)	Determination of Inorganic Anions by Ion Chromatography	Vol IC Chap 5	9056 Rev 0 9/94

SW-846 METHOD STATUS TABLE (3/95), CONTINUED

METH NO. THIRD ED DATED 9/86	METH NO. FINAL UPDATE I DATED 7/92	METH NO. FIN. UP. II (9/94), IIA (8/93), & IIB (1/95)	METHOD TITLE	SW-846 VOLUME/ CHAPTER/ SECTION LOCATION	CURRENT PROMUL-GATED METHOD
9060	--	--	Total Organic Carbon	Vol IC Chap 5	9060 Rev 0 9/86
9065	--	--	Phenolics (Spectrophotometric, Manual 4-AAP with Distillation)	Vol IC Chap 5	9065 Rev 0 9/86
9066	--	--	Phenolics (Colorimetric, Automated 4-AAP with Distillation)	Vol IC Chap 5	9066 Rev 0 9/86
9067	--	--	Phenolics (Spectrophotometric, MBTH with Distillation)	Vol IC Chap 5	9067 Rev 0 9/86
9070	--	--	Total Recoverable Oil & Grease (Gravimetric, Separatory Funnel Extraction)	Vol IC Chap 5	9070 Rev 0 9/86
9071	--	9071A (Up. II)	Oil and Grease Extraction Method for Sludge and Sediment Samples	Vol IC Chap 5	9071A Rev 1 9/94
--	--	9075 (Up. II)	Test Method for Total Chlorine in New and Used Petroleum Products by X-Ray Fluorescence Spectrometry (XRF)	Vol IC Chap 5	9075 Rev 0 9/94

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METH NO. THIRD ED DATED 9/86	METH NO. FINAL UPDATE I DATED 7/92	METH NO. FIN. UP. II (9/94), IIA (8/93), & IIB (1/95)	METHOD TITLE	SW-846 VOLUME/ CHAPTER/ SECTION LOCATION	CURRENT PROMUL-GATED METHOD
--	--	9076 (Up. II)	Test Method for Total Chlorine in New and Used Petroleum Products by Oxidative Combustion and Microcoulometry	Vol IC Chap 5	9076 Rev 0 9/94
--	--	9077 (Up. II)	Test Methods for Total Chlorine in New and Used Petroleum Products (Field Test Kit Methods)	Vol IC Chap 5	9077 Rev 0 9/94
9080	--	--	Cation-Exchange Capacity of Soils (Ammonium Acetate)	Vol IC Chap 6	9080 Rev 0 9/86
9081	--	--	Cation-Exchange Capacity of Soils (Sodium Acetate)	Vol IC Chap 6	9081 Rev 0 9/86
9090	9090A	--	Compatibility Test for Wastes and Membrane Liners	Vol IC Chap 6	9090A Rev 1 7/92
9095	--	--	Paint Filter Liquids Test	Vol IC Chap 6	9095 Rev 0 9/86
--	--	9096 (Up. II)	Liquid Release Test (LRT) Procedure	Vol IC Chap 6	9096 Rev 0 9/94

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METH NO. THIRD ED DATED 9/86	METH NO. FINAL UPDATE I DATED 7/92	METH NO. FIN. UP. II (9/94), IIA (8/93), & IIB (1/95)	METHOD TITLE	SW-846 VOLUME/ CHAPTER/ SECTION LOCATION	CURRENT PROMUL-GATED METHOD
9100	--	--	Saturated Hydraulic Conductivity, Saturated Leachate Conductivity, and Intrinsic Permeability	Vol IC Chap 6	9100 Rev 0 9/86
9131	--	--	Total Coliform: Multiple Tube Fermentation Technique	Vol IC Chap 5	9131 Rev 0 9/86
9132	--	--	Total Coliform: Membrane Filter Technique	Vol IC Chap 5	9132 Rev 0 9/86
9200	--	--	Nitrate	Vol IC Chap 5	9200 Rev 0 9/86
9250	--	--	Chloride (Colorimetric, Automated Ferricyanide AAI)	Vol IC Chap 5	9250 Rev 0 9/86
9251	--	--	Chloride (Colorimetric, Automated Ferricyanide AAII)	Vol IC Chap 5	9251 Rev 0 9/86
9252	--	9252A (Up. II)	Chloride (Titrimetric, Mercuric Nitrate)	Vol IC Chap 5	9252A Rev 1 9/94
--	--	9253 (Up. II)	Chloride (Titrimetric, Silver Nitrate)	Vol IC Chap 5	9253 Rev 0 9/94

SW-846 METHOD STATUS TABLE (3/95), CONTINUED

METH NO. THIRD ED DATED 9/86	METH NO. FINAL UPDATE I DATED 7/92	METH NO. FIN. UP. II (9/94), IIA (8/93), & IIB (1/95)	METHOD TITLE	SW-846 VOLUME/ CHAPTER/ SECTION LOCATION	CURRENT PROMUL-GATED METHOD
9310	--	--	Gross Alpha and Gross Beta	Vol IC Chap 6	9310 Rev 0 9/86
9315	--	--	Alpha-Emitting Radium Isotopes	Vol IC Chap 6	9315 Rev 0 9/86
9320	--	--	Radium-228	Vol IC Chap 5	9320 Rev 0 9/86
HCN Test Method	HCN Test Method	HCN Test Method	Test Method to Determine Hydrogen Cyanide Released from Wastes	Vol IC Chap 7 Sec 7.3	Guidance Method Only
H_2S Test Method	H_2S Test Method	H_2S Test Method	Test Method to Determine Hydrogen Sulfide Released from Wastes	Vol IC Chap 7 Sec 7.3	Guidance Method Only

ABSTRACT

Test Methods for Evaluating Solid Waste, Physical/Chemical Methods (SW-846) provides test procedures and guidance which are recommended for use in conducting the evaluations and measurements needed to comply with the Resource Conservation and Recovery Act (RCRA), Public Law 94-580, as amended. These methods are approved by the U.S. Environmental Protection Agency for obtaining data to satisfy the requirements of 40 CFR Parts 122 through 270 promulgated under RCRA, as amended. This manual presents the state-of-the-art in routine analytical tested adapted for the RCRA program. It contains procedures for field and laboratory quality control, sampling, determining hazardous constituents in wastes, determining the hazardous characteristics of wastes (toxicity, ignitability, reactivity, and corrosivity), and for determining physical properties of wastes. It also contains guidance on how to select appropriate methods.

Several of the hazardous waste regulations under Subtitle C of RCRA require that specific testing methods described in SW-846 be employed for certain applications. Refer to 40 *Code of Federal Regulations* (CFR), Parts 260 through 270, for those specific requirements. Any reliable analytical method may be used to meet other requirements under Subtitle C of RCRA.

METHOD INDEX AND CONVERSION TABLE

Method Number, Third Edition	Chapter Number, Third Edition	Method Number, Second Edition	Current Revision Number
0010	Ten	0010	0
0020	Ten	0020	0
0030	Ten	0030	0
1010	Eight (8.1)	1010	0
1020	Eight (8.1)	1020	0
1110	Eight (8.2)	1110	0
1310	Eight (8.4)	1310	0
1320	Six	1320	0
1330	Six	1330	0
3005	Three	3005	0
3010	Three	3010	0
3020	Three	3020	0
3040	Three	3040	0
3050	Three	3050	0
3500	Four (4.2.1)	None (new method)	0
3510	Four (4.2.1)	3510	0
3520	Four (4.2.1)	3520	0
3540	Four (4.2.1)	3540	0
3550	Four (4.2.1)	3550	0
3580	Four (4.2.1)	None (new method)	0
3600	Four (4.2.2)	None (new method)	0
3610	Four (4.2.2)	None (new method)	0
3611	Four (4.2.2)	3570	0
3620	Four (4.2.2)	None (new method)	0
3630	Four (4.2.2)	None (new method)	0
3640	Four (4.2.2)	None (new method)	0
3650	Four (4.2.2)	None (new method)	0
3660	Four (4.2.2)	None (new method)	0
3810	Four (4.4)	5020	0
3820	Four (4.4)	None (new method)	0
5030	Four (4.2.1)	5030	0
5040	Four (4.2.1)	3720	0
6010	Three	6010	0
7000	Three	7000	0
7020	Three	7020	0

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Date September 1986

METHOD INDEX AND CONVERSION TABLE
(Continued)

Method Number, Third Edition	Chapter Number, Third Edition	Method Number, Second Edition	Current Revision Number
7040	Three	7040	0
7041	Three	7041	0
7060	Three	7060	0
7061	Three	7061	0
7080	Three	7080	0
7090	Three	7090	0
7091	Three	7091	0
7130	Three	7130	0
7131	Three	7131	0
7140	Three	7140	0
7190	Three	7190	0
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7550	Three	7550	0
7610	Three	7610	0
7740	Three	7740	0
7741	Three	7741	0
7760	Three	7760	0
7770	Three	7770	0

METHOD INDEX AND CONVERSION TABLE
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Method Number, Third Edition	Chapter Number, Third Edition	Method Number, Second Edition	Current Revision Number
7840	Three	7840	0
7841	Three	7841	0
7870	Three	7870	0
7910	Three	7910	0
7911	Three	7911	0
7950	Three	7950	0
8000	Four (4.3.1)	None (new method)	0
8010	Four (4.3.1)	8010	0
8015	Four (4.3.1)	8015	0
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8030	Four (4.3.1)	8030	0
8040	Four (4.3.1)	8040	0
8060	Four (4.3.1)	8060	0
8080	Four (4.3.1)	8080	0
8090	Four (4.3.1)	8090	0
8100	Four (4.3.1)	8100	0
8120	Four (4.3.1)	8120	0
8140	Four (4.3.1)	8140	0
8150	Four (4.3.1)	8150	0
8240	Four (4.3.2)	8240	0
8250	Four (4.3.2)	8250	0
8270	Four (4.3.2)	8270	0
8280	Four (4.3.2)	None (new method)	0
8310	Four (4.3.3)	8310	0
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9022	Five	9022	0
9030	Five	9030	0
9035	Five	9035	0
9036	Five	9036	0
9038	Five	9038	0
9040	Six	9040	0
9041	Six	9041	0
9045	Six	9045	0
9050	Six	9050	0

METHOD INDEX AND CONVERSION TABLE
(Continued)

Method Number, Third Edition	Chapter Number, Third Edition	Method Number, Second Edition	Current Revision Number
9060	Five	9060	0
9065	Five	9065	0
9066	Five	9066	0
9067	Five	9067	0
9070	Five	9070	0
9071	Five	9071	0
9080	Six	9080	0
9081	Six	9081	0
9090	Six	9090	0
9095	Six	9095	0
9100	Six	9100	0
9131	Five	9131	0
9132	Five	9132	0
9200	Five	9200	0
9250	Five	9250	0
9251	Five	9251	0
9252	Five	9252	0
9310	Six	9310	0
9315	Six	9315	0
9320	Five	9320	0
HCN Test Method	Seven	HCN Test Method	0
H_2S Test Method	Seven	H_2S Test Method	0

PREFACE AND OVERVIEW

PURPOSE OF THE MANUAL

Test Methods for Evaluating Solid Waste (SW-846) is intended to provide a unified, up-to-date source of information on sampling and analysis related to compliance with RCRA regulations. It brings together into one reference all sampling and testing methodology approved by the Office of Solid Waste for use in implementing the RCRA regulatory program. The manual provides methodology for collecting and testing representative samples of waste and other materials to be monitored. Aspects of sampling and testing covered in SW-846 include quality control, sampling plan development and implementation, analysis of inorganic and organic constituents, the estimation of intrinsic physical properties, and the appraisal of waste characteristics.

The procedures described in this manual are meant to be comprehensive and detailed, coupled with the realization that the problems encountered in sampling and analytical situations require a certain amount of flexibility. The solutions to these problems will depend, in part, on the skill, training, and experience of the analyst. For some situations, it is possible to use this manual in rote fashion. In other situations, it will require a combination of technical abilities, using the manual as guidance rather than in a step-by-step, word-by-word fashion. Although this puts an extra burden on the user, it is unavoidable because of the variety of sampling and analytical conditions found with hazardous wastes.

ORGANIZATION AND FORMAT

This manual is divided into two volumes. Volume I focuses on laboratory activities and is divided for convenience into three sections. Volume IA deals with quality control, selection of appropriate test methods, and analytical methods for metallic species. Volume IB consists of methods for organic analytes. Volume IC includes a variety of test methods for miscellaneous analytes and properties for use in evaluating the waste characteristics. Volume II deals with sample acquisition and includes quality control, sampling plan design and implementation, and field sampling methods. Included for the convenience of sampling personnel are discusssions of the ground water, land treatment, and incineration monitoring regulations.

Volume I begins with an overview of the quality control precedures to be imposed upon the sampling and analytical methods. The quality control chapter (Chapter One) and the methods chapters are interdependent. The analytical procedures cannot be used without a thorough understanding of the quality control requirements and the means to implement them. This understanding can be achieved only be reviewing Chapter One and the analytical methods together. It is expected that individual laboratories, using SW-846 as the reference

source, will select appropriate methods and develop a standard operating procedure (SOP) to be followed by the laboratory. The SOP should incorporate the pertinent information from this manual adopted to the specific needs and circumstances of the individual laboratory as well as to the materials to be evaluated.

The method selection chapter (Chapter Two) presents a comprehensive discussion of the application of these methods to various matrices in the determination of groups of analytes or specific analytes. It aids the chemist in constructing the correct analytical method from the array of procedures which may cover the matrix/analyte/concentration combination of interests. The section discusses the objective of the testing program and its relationship to the choice of an analytical method. Flow charts are presented along with tables to guide in the selection of the correct analytical procedures to form the appropriate method.

The analytical methods are separated into distinct procedures describing specific, independent analytical operations. These include extraction, digestion, cleanup, and determination. This format allows linking of the various steps in the analysis according to: the type of sample (e.g., water, soil, sludge, still bottom); analytes(s) of interest; needed sensitivity; and available analytical instrumentation.. The chapters describing Miscellaneous Test Methods and Properties, however, give complete methods which are not amenable to such segmentation to form discrete procedures.

The introductory material at the beginning of each section containing analytical procedures presents information on sample handling and preservation, safety, and sample preparation.

Part II of Volume I (Chapters Seven and Eight) describes the characteristics of a waste. Sections following the regulatory descriptions contain the methods used to determine if the waste is hazardous because it exhibits a particular characteristic.

Volume II gives background information on statistical and nonstatistical aspects of sampling. It also presents practical sampling techniques appropriate for situations presenting a variety of physical conditions.

A discussion of the regulatory requirements with respect to several monitoring categories is also given in this volume. These include ground water monitoring, land treatment, and incineration. The purpose of this guidance is to orient the user to the objective of the analysis, and to assist in developing data quality objectives, sampling plans, and laboratory SOP's.

Significant interferences, or other problems, may be encountered with certain samples. In these situations, the analyst is advised to contact the Chief, Methods Section (WH-562B) Technical Assessment Branch, Office of Solid Waste, US EPA, Washington, DC 20460 (202-382-4761) for assistance. The manual is intended to serve all those with a need to evaluate solid waste. Your comments, corrections, suggestions, and questions concerning any material contained in, or omitted from, this manual will be gratefully appreciated. Please direct your comments to the above address.

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PART I METHODS FOR ANALYTES AND PROPERTIES

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CHAPTER ONE
QUALITY CONTROL

1.0 INTRODUCTION

It is the goal of the U.S. Environmental Protection Agency's (EPA's) quality assurance (QA) program to ensure that all data be scientifically valid, defensible, and of known precision and accuracy. The data should be of sufficient known quality to withstand scientific and legal challenge relative to the use for which the data are obtained. The QA program is management's tool for achieving this goal.

For RCRA analyses, the recommended minimum requirements for a QA program and the associated quality control (QC) procedures are provided in this chapter.

The data acquired from QC procedures are used to estimate the quality of analytical data, to determine the need for corrective action in response to identified deficiencies, and to interpret results after corrective action procedures are implemented. Method-specific QC procedures are incorporated in the individual methods since they are not applied universally.

A total program to generate data of acceptable quality should include both a QA component, which encompasses the management procedures and controls, as well as an operational day-to-day QC component. This chapter defines fundamental elements of such a data collection program. Data collection efforts involve:

1. design of a project plan to achieve the data quality objectives (DQOs);

2. implementation of the project plan; and

3. assessment of the data to determine if the DQOs are met.

The project plan may be a sampling and analysis plan or a waste analysis plan if it covers the QA/QC goals of the Chapter, or it may be a Quality Assurance Project Plan as described later in this chapter.

This chapter identifies the minimal QC components that should be used in the performance of sampling and analyses, including the QC information which should be documented. Guidance is provided to construct QA programs for field and laboratory work conducted in support of the RCRA program.

2.0 QA PROJECT PLAN

It is recommended that all projects which generate environment-related data in support of RCRA have a QA Project Plan (QAPjP) or equivalent. In some instances, a sampling and analysis plan or a waste analysis plan may be equivalent if it covers all of the QA/QC goals outlined in this chapter. In addition, a separate QAPjP need not be prepared for routine analyses or activities where the procedures to be followed are described in a Standard

Operating Procedures manual or similar document and include the elements of a QAPjP. These documents should be available and referenced in the documentation and/or records for the analysis activities. The term "QAPjP" in this chapter refers to any of these QA/QC documents.

The QAPjP should detail the QA/QC goals and protocols for a specific data collection activity. The QAPjP sets forth a plan for sampling and analysis activities that will generate data of a quality commensurate with their intended use. QAPjP elements should include a description of the project and its objectives; a statement of the DQOs of the project; identification of those involved in the data collection and their responsibilities and authorities; reference to (or inclusion of) the specific sample collection and analysis procedures that will be followed for all aspects of the project; enumeration of QC procedures to be followed; and descriptions of all project documentation. Additional elements should be included in the QAPjP if needed to address all quality related aspects of the data collection project. Elements should be omitted only when they are inappropriate for the project or when absence of those elements will not affect the quality of data obtained for the project (see reference 1).

The role and importance of DQOs and project documentation are discussed below in Sections 2.1 through 2.6. Management and organization play a critical role in determining the effectiveness of a QA/QC program and ensuring that all required procedures are followed. Section 2.7 discusses the elements of an organization's QA program that have been found to ensure an effective program. Field operations and laboratory operations (along with applicable QC procedures) are discussed in Sections 3 and 4, respectively.

2.1 DATA QUALITY OBJECTIVES

Data quality objectives (DQOs) for the data collection activity describe the overall level of uncertainty that a decision-maker is willing to accept in results derived from environmental data. This uncertainty is used to specify the quality of the measurement data required, usually in terms of objectives for precision, bias, representativeness, comparability and completeness. The DQOs should be defined prior to the initiation of the field and laboratory work. The field and laboratory organizations performing the work should be aware of the DQOs so that their personnel may make informed decisions during the course of the project to attain those DQOs. More detailed information on DQOs is available from the U.S. EPA Quality Assurance Management Staff (QAMS) (see references 2 and 4).

2.2 PROJECT OBJECTIVES

A statement of the project objectives and how the objectives are to be attained should be concisely stated and sufficiently detailed to permit clear understanding by all parties involved in the data collection effort. This includes a statement of what problem is to be solved and the information required

in the process. It also includes appropriate statements of the DQOs (i.e., the acceptable level of uncertainty in the information).

2.3 SAMPLE COLLECTION

Sampling procedures, locations, equipment, and sample preservation and handling requirements should be specified in the QAPjP. Further details on quality assurance procedures for field operations are described in Section 3 of this chapter. The OSW is developing policies and procedures for sampling in a planned revision of Chapter Nine of this manual. Specific procedures for groundwater sampling are provided in Chapter Eleven of this manual.

2.4 ANALYSIS AND TESTING

Analytes and properties of concern, analytical and testing procedures to be employed, required detection limits, and requirements for precision and bias should be specified. All applicable regulatory requirements and the project DQOs should be considered when developing the specifications. Further details on the procedures for analytical operations are described in Section 4 of this chapter.

2.5 QUALITY CONTROL

The quality assurance program should address both field and laboratory activities. Quality control procedures should be specified for estimating the precision and bias of the data. Recommended minimum requirements for QC samples have been established by EPA and should be met in order to satisfy recommended minimum criteria for acceptable data quality. Further details on procedures for field and laboratory operations are described in Sections 3 and 4, respectively, of this chapter.

2.6 PROJECT DOCUMENTATION

Documents should be prepared and maintained in conjunction with the data collection effort. Project documentation should be sufficient to allow review of all aspects of the work being performed. The QAPjP discussed in Sections 3 and 4 is one important document that should be maintained.

The length of storage time for project records should comply with regulatory requirements, organizational policy, or project requirements, whichever is more stringent. It is recommended that documentation be stored for three years from submission of the project final report.

Documentation should be secured in a facility that adequately addresses/minimizes its deterioration for the length of time that it is to be retained. A system allowing for the expedient retrieval of information should exist.

Access to archived information should be controlled to maintain the integrity of the data. Procedures should be developed to identify those individuals with access to the data.

2.7 ORGANIZATION PERFORMING FIELD OR LABORATORY OPERATIONS

Proper design and structure of the organization facilitates effective and efficient transfer of information and helps to prevent important procedures from being overlooked.

The organizational structure, functional responsibilities, levels of authority, job descriptions, and lines of communication for all project activities should be established and documented. One person may cover more than one organizational function. Each project participant should have a clear understanding of his or her duties and responsibilities and the relationship of those responsibilities to the overall data collection effort.

The management of each organization participating in a project involving data collection activities should establish that organization's operational and QA policies. This information should be documented in the QAPjP. The management should ensure that (1) the appropriate methodologies are followed as documented in the QAPjPs; (2) personnel clearly understand their duties and responsibilities; (3) each staff member has access to appropriate project documents; (4) any deviations from the QAPjP are communicated to the project management and documented; and (5) communication occurs between the field, laboratory, and project management, as specified in the QAPjP. In addition, each organization should ensure that their activities do not increase the risk to humans or the environment at or about the project location. Certain projects may require specific policies or a Health and Safety Plan to provide this assurance.

The management of the participating field or laboratory organization should establish personnel qualifications and training requirements for the project. Each person participating in the project should have the education, training, technical knowledge, and experience, or a combination thereof, to enable that individual to perform assigned functions. Training should be provided for each staff member as necessary to perform their functions properly. Personnel qualifications should be documented in terms of education, experience, and training, and periodically reviewed to ensure adequacy to current responsibilities.

Each participating field organization or laboratory organization should have a designated QA function (i.e., a team or individual trained in QA) to monitor operations to ensure that the equipment, personnel, activities, procedures, and documentation conform with the QAPjP. To the extent possible, the QA monitoring function should be entirely separate from, and independent of, personnel engaged in the work being monitored. The QA function should be responsible for the QA review.

2.7.1 Performance Evaluation

Performance evaluation studies are used to measure the performance of the laboratory on unknown samples. Performance evaluation samples are typically submitted to the laboratory as blind samples by an independent outside source. The results are compared to predetermined acceptance limits. Performance evaluation samples can also be submitted to the laboratory as part of the QA function during internal assessment of laboratory performance. Records of all performance evaluation studies should be maintained by the laboratory. Problems identified through participation in performance evaluation studies should be immediately investigated and corrected.

2.7.2 Internal Assessment by QA Function

Personnel performing field and laboratory activities are responsible for continually monitoring individual compliance with the QAPjP. The QA function should review procedures, results and calculations to determine compliance with the QAPjP. The results of this internal assessment should be reported to management with requirements for a plan to correct observed deficiencies.

2.7.3 External Assessment

The field and laboratory activities may be reviewed by personnel external to the organization. Such an assessment is an extremely valuable method for identifying overlooked problems. The results of the external assessment should be submitted to management with requirements for a plan to correct observed deficiencies.

2.7.4 On-Site Evaluation

On-site evaluations may be conducted as part of both internal and external assessments. The focus of an on-site evaluation is to evaluate the degree of conformance of project activities with the applicable QAPjP. On-site evaluations may include, but are not limited to, a complete review of facilities, staff, training, instrumentation, procedures, methods, sample collection, analyses, QA policies and procedures related to the generation of environmental data. Records of each evaluation should include the date of the evaluation, location, the areas reviewed, the person performing the evaluation, findings and problems, and actions recommended and taken to resolve problems. Any problems identified that are likely to affect data integrity should be brought immediately to the attention of management.

2.7.4.1 Field Activities

The review of field activities should be conducted by one or more persons knowledgeable in the activities being reviewed and include evaluating, at a minimum, the following subjects:

Completeness of Field Reports -- This review determines whether all requirements for field activities in the QAPjP have been fulfilled, that complete records exist for each field activity, and that the procedures

specified in the QAPjP have been implemented. Emphasis on field documentation will help assure sample integrity and sufficient technical information to recreate each field event. The results of this completeness check should be documented, and environmental data affected by incomplete records should be identified.

Identification of Valid Samples -- This review involves interpretation and evaluation of the field records to detect problems affecting the representativeness of environmental samples. Examples of items that might indicate potentially invalid samples include improper well development, improperly screened wells, instability of pH or conductivity, and collection of volatiles near internal combustion engines. The field records should be evaluated against the QAPjP and SOPs. The reviewer should document the sample validity and identify the environmental data associated with any poor or incorrect field work.

Correlation of Field Test Data -- This review involves comparing any available results of field measurements obtained by more than one method. For example, surface geophysical methods should correlate with direct methods of site geologic characterization such as lithologic logs constructed during drilling operations.

Identification of Anomalous Field Test Data -- This review identifies any anomalous field test data. For example, a water temperature for one well that is 5 degrees higher than any other well temperature in the same aquifer should be noted. The reviewer should evaluate the impact of anomalous field measurement results on the associated environmental data.

Validation of Field Analyses -- This review validates and documents all data from field analysis that are generated in situ or from a mobile laboratory as specified in Section 2.7.4.2. The reviewer should document whether the QC checks meet the acceptance criteria, and whether corrective actions were taken for any analysis performed when acceptance criteria were exceeded.

2.7.4.2 Laboratory Activities

The review of laboratory data should be conducted by one or more persons knowledgeable in laboratory activities and include evaluating, at a minimum, the following subjects:

Completeness of Laboratory Records -- This review determines whether: (1) all samples and analyses required by the QAPjP have been processed, (2) complete records exist for each analysis and the associated QC samples, and that (3) the procedures specified in the QAPjP have been implemented. The results of the completeness check should be documented, and environmental data affected by incomplete records should be identified.

Evaluation of Data with Respect to Detection and Quantitation Limits -- This review compares analytical results to required quantitation limits. Reviewers should document instances where detection or quantitation limits

exceed regulatory limits, action levels, or target concentrations specified in the QAPjP.

Evaluation of Data with Respect to Control Limits -- This review compares the results of QC and calibration check samples to control criteria. Corrective action should be implemented for data not within control limits. The reviewer should check that corrective action reports, and the results of reanalysis, are available. The review should determine whether samples associated with out-of-control QC data are identified in a written record of the data review, and whether an assessment of the utility of such analytical results is recorded.

Review of Holding Time Data -- This review compares sample holding times to those required by the QAPjP, and notes all deviations.

Review of Performance Evaluation (PE) Results -- PE study results can be helpful in evaluating the impact of out-of-control conditions. This review documents any recurring trends or problems evident in PE studies and evaluates their effect on environmental data.

Correlation of Laboratory Data -- This review determines whether the results of data obtained from related laboratory tests, e.g., Purgeable Organic Halides (POX) and Volatile Organics, are documented, and whether the significance of any differences is discussed in the reports.

2.7.5 QA Reports

There should be periodic reporting of pertinent QA/QC information to the project management to allow assessment of the overall effectiveness of the QA program. There are three major types of QA reports to project management:

Periodic Report on Key QA Activities -- Provides summary of key QA activities during the period, stressing measures that are being taken to improve data quality; describes significant quality problems observed and corrective actions taken; reports information regarding any changes in certification/accreditation status; describes involvement in resolution of quality issues with clients or agencies; reports any QA organizational changes; and provides notice of the distribution of revised documents controlled by the QA organization (i.e., procedures).

Report on Measurement Quality Indicators -- Includes the assessment of QC data gathered over the period, the frequency of analyses repeated due to unacceptable QC performance, and, if possible, the reason for the unacceptable performance and corrective action taken.

Reports on QA Assessments -- Includes the results of the assessments and the plan for correcting identified deficiencies; submitted immediately following any internal or external on-site evaluation or upon receipt of the results of any performance evaluation studies.

3.0 FIELD OPERATIONS

The field operations should be conducted in such a way as to provide reliable information that meets the DQOs. To achieve this, certain minimal policies and procedures should be implemented. The OSW is considering revisions of Chapter Nine and Eleven of this manual. Supplemental information and guidance is available in the RCRA Ground-Water Monitoring Technical Enforcement Guidance Document (TEGD) (Reference 3). The project documentation should contain the information specified below.

3.1 FIELD LOGISTICS

The QAPjP should describe the type(s) of field operations to be performed and the appropriate area(s) in which to perform the work. The QAPjP should address ventilation, protection from extreme weather and temperatures, access to stable power, and provision for water and gases of required purity.

Whenever practical, the sampling site facilities should be examined prior to the start of work to ensure that all required items are available. The actual area of sampling should be examined to ensure that trucks, drilling equipment, and personnel have adequate access to the site.

The determination as to whether sample shipping is necessary should be made during planning for the project. This need is established by evaluating the analyses to be performed, sample holding times, and location of the site and the laboratory. Shipping or transporting of samples to a laboratory should be done within a timeframe such that recommended holding times are met.

Samples should be packaged, labelled, preserved (e.g., preservative added, iced, etc.), and documented in an area which is free of contamination and provides for secure storage. The level of custody and whether sample storage is needed should be addressed in the QAPjP.

Storage areas for solvents, reagents, standards, and reference materials should be adequate to preserve their identity, concentration, purity, and stability prior to use.

Decontamination of sampling equipment may be performed at the location where sampling occurs, prior to going to the sampling site, or in designated areas near the sampling site. Project documentation should specify where and how this work is accomplished. If decontamination is to be done at the site, water and solvents of appropriate purity should be available. The method of accomplishing decontamination, including the required materials, solvents, and water purity should be specified.

During the sampling process and during on-site or <u>in situ</u> analyses, waste materials are sometimes generated. The method for storage and disposal of these waste materials that complies with applicable local, state and Federal regulations should be specified. Adequate facilities should be provided for the collection and storage of all wastes, and these facilities should be operated so

as to minimize environmental contamination. Waste storage and disposal facilities should comply with applicable federal, state, and local regulations.

The location of long-term and short-term storage for field records, and the measures to ensure the integrity of the data should be specified.

3.2 EQUIPMENT/INSTRUMENTATION

The equipment, instrumentation, and supplies at the sampling site should be specified and should be appropriate to accomplish the activities planned. The equipment and instrumentation should meet the requirements of specifications, methods, and procedures as specified in the QAPjP.

3.3 OPERATING PROCEDURES

The QAPjP should describe or make reference to all field activities that may affect data quality. For routinely performed activities, standard operating procedures (SOPs) are often prepared to ensure consistency and to save time and effort in preparing QAPjPs. Any deviation from an established procedure during a data collection activity should be documented. The procedures should be available for the indicated activities, and should include, at a minimum, the information described below.

3.3.1 Sample Management

The numbering and labeling system, chain-of-custody procedures, and how the samples are to be tracked from collection to shipment or receipt by the laboratory should be specified. Sample management procedures should also specify the holding times, volumes of sample required by the laboratory, required preservatives, and shipping requirements.

3.3.2 Reagent/Standard Preparation

The procedures describing how to prepare standards and reagents should be specified. Information concerning specific grades of materials used in reagent and standard preparation, appropriate glassware and containers for preparation and storage, and labeling and record keeping for stocks and dilutions should be included.

3.3.3 Decontamination

The procedures describing decontamination of field equipment before and during the sample collection process should be specified. These procedures should include cleaning materials used, the order of washing and rinsing with the cleaning materials, requirements for protecting or covering cleaned equipment, and procedures for disposing of cleaning materials.

3.3.4 Sample Collection

The procedures describing how the sampling operations are actually performed in the field should be specified. A simple reference to standard methods is not sufficient, unless a procedure is performed exactly as described in the published method. Methods from source documents published by the EPA, American Society for Testing and Materials, U.S. Department of the Interior, National Water Well Association, American Petroleum Institute, or other recognized organizations with appropriate expertise should be used, if possible. The procedures for sample collection should include at least the following:

- Applicability of the procedure,
- Equipment required,
- Detailed description of procedures to be followed in collecting the samples,
- Common problems encountered and corrective actions to be followed, and
- Precautions to be taken.

3.3.5 Field Measurements

The procedures describing all methods used in the field to determine a chemical or physical parameter should be described in detail. The procedures should address criteria from Section 4, as appropriate.

3.3.6 Equipment Calibration And Maintenance

The procedures describing how to ensure that field equipment and instrumentation are in working order should be specified. These describe calibration procedures and schedules, maintenance procedures and schedules, maintenance logs, and service arrangements for equipment. Calibration and maintenance of field equipment and instrumentation should be in accordance with manufacturers' specifications or applicable test specifications and should be documented.

3.3.7 Corrective Action

The procedures describing how to identify and correct deficiencies in the sample collection process should be specified. These should include specific steps to take in correcting deficiencies such as performing additional decontamination of equipment, resampling, or additional training of field personnel. The procedures should specify that each corrective action should be documented with a description of the deficiency and the corrective action taken, and should include the person(s) responsible for implementing the corrective action.

3.3.8 Data Reduction and Validation

The procedures describing how to compute results from field measurements and to review and validate these data should be specified. They should include all formulas used to calculate results and procedures used to independently verify that field measurement results are correct.

3.3.9 Reporting

The procedures describing the process for reporting the results of field activities should be specified.

3.3.10 Records Management

The procedures describing the means for generating, controlling, and archiving project-specific records and field operations records should be specified. These procedures should detail record generation and control and the requirements for record retention, including type, time, security, and retrieval and disposal authorities.

Project-specific records relate to field work performed for a project. These records may include correspondence, chain-of-custody records, field notes, all reports issued as a result of the work, and procedures used.

Field operations records document overall field operations and may include equipment performance and maintenance logs, personnel files, general field procedures, and corrective action reports.

3.3.11 Waste Disposal

The procedures describing the methods for disposal of waste materials resulting from field operations should be specified.

3.4 FIELD QA AND QC REQUIREMENTS

The QAPjP should describe how the following elements of the field QC program will be implemented.

3.4.1 Control Samples

Control samples are QC samples that are introduced into a process to monitor the performance of the system. Control samples, which may include blanks (e.g., trip, equipment, and laboratory), duplicates, spikes, analytical standards, and reference materials, can be used in different phases of the data collection process beginning with sampling and continuing through transportation, storage, and analysis.

Each day of sampling, at least one field duplicate and one equipment rinsate should be collected for each matrix sampled. If this frequency is not appropriate for the sampling equipment and method, then the appropriate changes

should be clearly identified in the QAPjP. When samples are collected for volatile organic analysis, a trip blank is also recommended for each day that samples are collected. In addition, for each sampling batch (20 samples of one matrix type), enough volume should be collected for at least one sample so as to allow the laboratory to prepare one matrix spike and either one matrix duplicate or one matrix spike duplicate for each analytical method employed. This means that the following control samples are recommended:

- Field duplicate (one per day per matrix type)
- Equipment rinsate (one per day per matrix type)
- Trip blank (one per day, volatile organics only)
- Matrix spike (one per batch [20 samples of each matrix type])
- Matrix duplicate or matrix spike duplicate (one per batch)

Additional control samples may be necessary in order to assure data quality to meet the project-specific DQOs.

3.4.2 Acceptance Criteria

Procedures should be in place for establishing acceptance criteria for field activities described in the QAPjP. Acceptance criteria may be qualitative or quantitative. Field events or data that fall outside of established acceptance criteria may indicate a problem with the sampling process that should be investigated.

3.4.3 Deviations

All deviations from plan should be documented as to the extent of, and reason for, the deviation. Any activity not performed in accordance with procedures or QAPjPs is considered a deviation from plan. Deviations from plan may or may not affect data quality.

3.4.4 Corrective Action

Errors, deficiencies, deviations, certain field events, or data that fall outside established acceptance criteria should be investigated. In some instances, corrective action may be needed to resolve the problem and restore proper functioning to the system. The investigation of the problem and any subsequent corrective action taken should be documented.

3.4.5 Data Handling

All field measurement data should be reduced according to protocols described or referenced in the QAPjP. Computer programs used for data reduction should be validated before use and verified on a regular basis. All information used in the calculations should be recorded to enable reconstruction of the final result at a later date.

Data should be reported in accordance with the requirements of the end-user as described in the QAPjP.

3.5 QUALITY ASSURANCE REVIEW

The QA Review consists of internal and external assessments to ensure that QA/QC procedures are in use and to ensure that field staff conform to these procedures. QA review should be conducted as deemed appropriate and necessary.

3.6 FIELD RECORDS

Records provide the direct evidence and support for the necessary technical interpretations, judgments, and discussions concerning project activities. These records, particularly those that are anticipated to be used as evidentiary data, should directly support current or ongoing technical studies and activities and should provide the historical evidence needed for later reviews and analyses. Records should be legible, identifiable, and retrievable and protected against damage, deterioration, or loss. The discussion in this section (3.6) outlines recommended procedures for record keeping. Organizations which conduct field sampling should develop appropriate record keeping procedures which satisfy relevant technical and legal requirements.

Field records generally consist of bound field notebooks with prenumbered pages, sample collection forms, personnel qualification and training forms, sample location maps, equipment maintenance and calibration forms, chain-of-custody forms, sample analysis request forms, and field change request forms. All records should be written in indelible ink.

Procedures for reviewing, approving, and revising field records should be clearly defined, with the lines of authority included. It is recommended that all documentation errors should be corrected by drawing a single line through the error so it remains legible and should be initialed by the responsible individual, along with the date of change. The correction should be written adjacent to the error.

Records should include (but are not limited to) the following:

Calibration Records & Traceability of Standards/Reagents -- Calibration is a reproducible reference point to which all sample measurements can be correlated. A sound calibration program should include provisions for documentation of frequency, conditions, standards, and records reflecting the calibration history of a measurement system. The accuracy of the calibration standards is important because all data will be in reference to the standards used. A program for verifying and documenting the accuracy of all working standards against primary grade standards should be routinely followed.

Sample Collection -- To ensure maximum utility of the sampling effort and resulting data, documentation of the sampling protocol, as performed in the field, is essential. It is recommended that sample collection records contain, at a minimum, the names of persons conducting the activity, sample number, sample location, equipment used, climatic conditions, documentation of adherence to protocol, and unusual observations. The

actual sample collection record is usually one of the following: a bound field notebook with prenumbered pages, a pre-printed form, or digitized information on a computer tape or disc.

Chain-of-Custody Records -- The chain-of-custody involving the possession of samples from the time they are obtained until they are disposed or shipped off-site should be documented as specified in the QAPjP and should include the following information: (1) the project name; (2) signatures of samplers; (3) the sample number, date and time of collection, and grab or composite sample designation; (4) signatures of individuals involved in sample transfer; and (5) if applicable, the air bill or other shipping number.

Maps and Drawings -- Project planning documents and reports often contain maps. The maps are used to document the location of sample collection points and monitoring wells and as a means of presenting environmental data. Information used to prepare maps and drawings is normally obtained through field surveys, property surveys, surveys of monitoring wells, aerial photography or photogrammetric mapping. The final, approved maps and/or drawings should have a revision number and date and should be subject to the same controls as other project records.

QC Samples -- Documentation for generation of QC samples, such as trip and equipment rinsate blanks, duplicate samples, and any field spikes should be maintained.

Deviations -- All deviations from procedural documents and the QAPjP should be recorded in the site logbook.

Reports -- A copy of any report issued and any supporting documentation should be retained.

4.0 LABORATORY OPERATIONS

The laboratory should conduct its operations in such a way as to provide reliable information. To achieve this, certain minimal policies and procedures should be implemented.

4.1 FACILITIES

The QAPjP should address all facility-related issues that may impact project data quality. Each laboratory should be of suitable size and construction to facilitate the proper conduct of the analyses. Adequate bench space or working area per analyst should be provided. The space requirement per analyst depends on the equipment or apparatus that is being utilized, the number of samples that the analyst is expected to handle at any one time, and the number of operations that are to be performed concurrently by a single analyst. Other issues to be considered include, but are not limited to, ventilation, lighting,

control of dust and drafts, protection from extreme temperatures, and access to a source of stable power.

Laboratories should be designed so that there is adequate separation of functions to ensure that no laboratory activity has an adverse effect on the analyses. The laboratory may require specialized facilities such as a perchloric acid hood or glovebox.

Separate space for laboratory operations and appropriate ancillary support should be provided, as needed, for the performance of routine and specialized procedures.

As necessary to ensure secure storage and prevent contamination or misidentification, there should be adequate facilities for receipt and storage of samples. The level of custody required and any special requirements for storage such as refrigeration should be described in planning documents.

Storage areas for reagents, solvents, standards, and reference materials should be adequate to preserve their identity, concentration, purity, and stability.

Adequate facilities should be provided for the collection and storage of all wastes, and these facilities should be operated so as to minimize environmental contamination. Waste storage and disposal facilities should comply with applicable federal, state, and local regulations.

The location of long-term and short-term storage of laboratory records and the measures to ensure the integrity of the data should be specified.

4.2 EQUIPMENT/INSTRUMENTATION

Equipment and instrumentation should meet the requirements and specifications of the specific test methods and other procedures as specified in the QAPjP. The laboratory should maintain an equipment/instrument description list that includes the manufacturer, model number, year of purchase, accessories, and any modifications, updates, or upgrades that have been made.

4.3 OPERATING PROCEDURES

The QAPjP should describe or make reference to all laboratory activities that may affect data quality. For routinely performed activities, SOPs are often prepared to ensure consistency and to save time and effort in preparing QAPjPs. Any deviation from an established procedure during a data collection activity should be documented. It is recommended that procedures be available for the indicated activities, and include, at a minimum, the information described below.

4.3.1 Sample Management

The procedures describing the receipt, handling, scheduling, and storage of samples should be specified.

Sample Receipt and Handling -- These procedures describe the precautions to be used in opening sample shipment containers and how to verify that chain-of-custody has been maintained, examine samples for damage, check for proper preservatives and temperature, and log samples into the laboratory sample streams.

Sample Scheduling -- These procedures describe the sample scheduling in the laboratory and includes procedures used to ensure that holding time requirements are met.

Sample Storage -- These procedures describe the storage conditions for all samples, verification and documentation of daily storage temperature, and how to ensure that custody of the samples is maintained while in the laboratory.

4.3.2 Reagent/Standard Preparation

The procedures describing how to prepare standards and reagents should be specified. Information concerning specific grades of materials used in reagent and standard preparation, appropriate glassware and containers for preparation and storage, and labeling and recordkeeping for stocks and dilutions should be included.

4.3.3 General Laboratory Techniques

The procedures describing all essentials of laboratory operations that are not addressed elsewhere should be specified. These techniques should include, but are not limited to, glassware cleaning procedures, operation of analytical balances, pipetting techniques, and use of volumetric glassware.

4.3.4 Test Methods

Procedures for test methods describing how the analyses are actually performed in the laboratory should be specified. A simple reference to standard methods is not sufficient, unless the analysis is performed exactly as described in the published method. Whenever methods from SW-846 are not appropriate, recognized methods from source documents published by the EPA, American Public Health Association (APHA), American Society for Testing and Materials (ASTM), the National Institute for Occupational Safety and Health (NIOSH), or other recognized organizations with appropriate expertise should be used, if possible. The documentation of the actual laboratory procedures for analytical methods should include the following:

Sample Preparation and Analysis Procedures -- These include applicable holding time, extraction, digestion, or preparation steps as appropriate to the method; procedures for determining the appropriate dilution to

analyze; and any other information required to perform the analysis accurately and consistently.

Instrument Standardization -- This includes concentration(s) and frequency of analysis of calibration standards, linear range of the method, and calibration acceptance criteria.

Sample Data -- This includes recording requirements and documentation including sample identification number, analyst, data verification, date of analysis and verification, and computational method(s).

Precision and Bias -- This includes all analytes for which the method is applicable and the conditions for use of this information.

Detection and Reporting Limits -- This includes all analytes in the method.

Test-Specific QC -- This describes QC activities applicable to the specific test and references any applicable QC procedures.

4.3.5 Equipment Calibration and Maintenance

The procedures describing how to ensure that laboratory equipment and instrumentation are in working order should be specified. These procedures include calibration procedures and schedules, maintenance procedures and schedules, maintenance logs, service arrangements for all equipment, and spare parts available in-house. Calibration and maintenance of laboratory equipment and instrumentation should be in accordance with manufacturers' specifications or applicable test specifications and should be documented.

4.3.6 QC

The type, purpose, and frequency of QC samples to be analyzed in the laboratory and the acceptance criteria should be specified. Information should include the applicability of the QC sample to the analytical process, the statistical treatment of the data, and the responsibility of laboratory staff and management in generating and using the data. Further details on development of project-specific QC protocols are described in Section 4.4.

4.3.7 Corrective Action

The procedures describing how to identify and correct deficiencies in the analytical process should be specified. These should include specific steps to take in correcting the deficiencies such as preparation of new standards and reagents, recalibration and restandardization of equipment, reanalysis of samples, or additional training of laboratory personnel in methods and procedures. The procedures should specify that each corrective action should be documented with a description of the deficiency and the corrective action taken, and should include the person(s) responsible for implementing the corrective action.

4.3.8 Data Reduction and Validation

The procedures describing how to review and validate the data should be specified. They should include procedures for computing and interpreting the results from QC samples, and independent procedures to verify that the analytical results are reported correctly. In addition, routine procedures used to monitor precision and bias, including evaluations of reagent, equipment rinsate, and trip blanks, calibration standards, control samples, duplicate and matrix spike samples, and surrogate recovery, should be detailed in the procedures. More detailed validation procedures should be performed when required in the contract or QAPjP.

4.3.9 Reporting

The procedures describing the process for reporting the analytical results should be specified.

4.3.10 Records Management

The procedures describing the means for generating, controlling, and archiving laboratory records should be specified. The procedures should detail record generation and control, and the requirements for record retention, including type, time, security, and retrieval and disposal authorities.

Project-specific records may include correspondence, chain-of-custody records, request for analysis, calibration data records, raw and finished analytical and QC data, data reports, and procedures used.

Laboratory operations records may include laboratory notebooks, instrument performance logs and maintenance logs in bound notebooks with prenumbered pages; laboratory benchsheets; software documentation; control charts; reference material certification; personnel files; laboratory procedures; and corrective action reports.

4.3.11 Waste Disposal

The procedures describing the methods for disposal of chemicals including standard and reagent solutions, process waste, and samples should be specified.

4.4 LABORATORY QA AND QC PROCEDURES

The QAPjP should describe how the following required elements of the laboratory QC program are to be implemented.

4.4.1 Method Proficiency

Procedures should be in place for demonstrating proficiency with each analytical method routinely used in the laboratory. These should include procedures for demonstrating the precision and bias of the method as performed by the laboratory and procedures for determining the method detection limit

(MDL). All terminology, procedures and frequency of determinations associated with the laboratory's establishment of the MDL and the reporting limit should be well-defined and well-documented. Documented precision, bias, and MDL information should be maintained for all methods performed in the laboratory.

4.4.2 Control Limits

Procedures should be in place for establishing and updating control limits for analysis. Control limits should be established to evaluate laboratory precision and bias based on the analysis of control samples. Typically, control limits for bias are based on the historical mean recovery plus or minus three standard deviation units, and control limits for precision range from zero (no difference between duplicate control samples) to the historical mean relative percent difference plus three standard deviation units. Procedures should be in place for monitoring historical performance and should include graphical (control charts) and/or tabular presentations of the data.

4.4.3 Laboratory Control Procedures

Procedures should be in place for demonstrating that the laboratory is in control during each data collection activity. Analytical data generated with laboratory control samples that fall within prescribed limits are judged to be generated while the laboratory was in control. Data generated with laboratory control samples that fall outside the established control limits are judged to be generated during an "out-of-control" situation. These data are considered suspect and should be repeated or reported with qualifiers.

Laboratory Control Samples -- Laboratory control samples should be analyzed for each analytical method when appropriate for the method. A laboratory control sample consists of either a control matrix spiked with analytes representative of the target analytes or a certified reference material.

Laboratory control sample(s) should be analyzed with each batch of samples processed to verify that the precision and bias of the analytical process are within control limits. The results of the laboratory control sample(s) are compared to control limits established for both precision and bias to determine usability of the data.

Method Blank -- When appropriate for the method, a method blank should be analyzed with each batch of samples processed to assess contamination levels in the laboratory. Guidelines should be in place for accepting or rejecting data based on the level of contamination in the blank.

Procedures should be in place for documenting the effect of the matrix on method performance. When appropriate for the method, there should be at least one matrix spike and either one matrix duplicate or one matrix spike duplicate per analytical batch. Additional control samples may be necessary to assure data quality to meet the project-specific DQOs.

Matrix-Specific Bias -- Procedures should be in place for determining the bias of the method due to the matrix. These procedures should include preparation and analysis of matrix spikes, selection and use of surrogates for organic methods, and the method of standard additions for metal and inorganic methods. When the concentration of the analyte in the sample is greater than 0.1%, no spike is necessary.

Matrix-Specific Precision -- Procedures should be in place for determining the precision of the method for a specific matrix. These procedures should include analysis of matrix duplicates and/or matrix spike duplicates. The frequency of use of these techniques should be based on the DQO for the data collection activity.

Matrix-Specific Detection Limit -- Procedures should be in place for determining the MDL for a specific matrix type (e.g., wastewater treatment sludge, contaminated soil, etc).

4.4.4 Deviations

Any activity not performed in accordance with laboratory procedures or QAPjPs is considered a deviation from plan. All deviations from plan should be documented as to the extent of, and reason for, the deviation.

4.4.5 Corrective Action

Errors, deficiencies, deviations, or laboratory events or data that fall outside of established acceptance criteria should be investigated. In some instances, corrective action may be needed to resolve the problem and restore proper functioning to the analytical system. The investigation of the problem and any subsequent corrective action taken should be documented.

4.4.6 Data Handling

Data resulting from the analyses of samples should be reduced according to protocols described in the laboratory procedures. Computer programs used for data reduction should be validated before use and verified on a regular basis. All information used in the calculations (e.g., raw data, calibration files, tuning records, results of standard additions, interference check results, and blank- or background-correction protocols) should be recorded in order to enable reconstruction of the final result at a later date. Information on the preparation of the sample (e.g., weight or volume of sample used, percent dry weight for solids, extract volume, dilution factor used) should also be maintained in order to enable reconstruction of the final result at a later date.

All data should be reviewed by a second analyst or supervisor according to laboratory procedures to ensure that calculations are correct and to detect transcription errors. Spot checks should be performed on computer calculations to verify program validity. Errors detected in the review process should be referred to the analyst(s) for corrective action. Data should be reported in accordance with the requirements of the end-user. It is recommended that the supporting documentation include at a minimum:

- Laboratory name and address.
- Sample information (including unique sample identification, sample collection date and time, date of sample receipt, and date(s) of sample preparation and analysis).
- Analytical results reported with an appropriate number of significant figures.
- Detection limits that reflect dilutions, interferences, or correction for equivalent dry weight.
- Method reference.
- Appropriate QC results (correlation with sample batch should be traceable and documented).
- Data qualifiers with appropriate references and narrative on the quality of the results.

4.5 QUALITY ASSURANCE REVIEW

The QA review consists of internal and external assessments to ensure that QA/QC procedures are in use and to ensure that laboratory staff conform to these procedures. QA review should be conducted as deemed appropriate and necessary.

4.6 LABORATORY RECORDS

Records provide the direct evidence and support for the necessary technical interpretations, judgements, and discussions concerning project activities. These records, particularly those that are anticipated to be used as evidentiary data, should directly support technical studies and activities, and provide the historical evidence needed for later reviews and analyses. Records should be legible, identifiable, and retrievable, and protected against damage, deterioration, or loss. The discussion in this section (4.6) outlines recommended procedures for record keeping. Organizations which conduct field sampling should develop appropriate record keeping procedures which satisfy relevant technical and legal requirements.

Laboratory records generally consist of bound notebooks with prenumbered pages, personnel qualification and training forms, equipment maintenance and calibration forms, chain-of-custody forms, sample analysis request forms, and analytical change request forms. All records should be written in indelible ink.

Procedures for reviewing, approving, and revising laboratory records should be clearly defined, with the lines of authority included. Any documentation errors should be corrected by drawing a single line through the error so that it remains legible and should be initialed by the responsible individual, along with the date of change. The correction is written adjacent to the error.

Strip-chart recorder printouts should be signed by the person who performed the instrumental analysis. If corrections need to be made in computerized data, a system parallel to the corrections for handwritten data should be in place.

Records of sample management should be available to permit the re-creation of an analytical event for review in the case of an audit or investigation of a dubious result.

Laboratory records should include, at least, the following:

Operating Procedures -- Procedures should be available to those performing the task outlined. Any revisions to laboratory procedures should be written, dated, and distributed to all affected individuals to ensure implementation of changes. Areas covered by operating procedures are given in Sections 3.3 and 4.3.

Quality Assurance Plans -- The QAPjP should be on file.

Equipment Maintenance Documentation -- A history of the maintenance record of each system serves as an indication of the adequacy of maintenance schedules and parts inventory. As appropriate, the maintenance guidelines of the equipment manufacturer should be followed. When maintenance is necessary, it should be documented in either standard forms or in logbooks. Maintenance procedures should be clearly defined and written for each measurement system and required support equipment.

Proficiency -- Proficiency information on all compounds reported should be maintained and should include (1) precision; (2) bias; (3) method detection limits; (4) spike recovery, where applicable; (5) surrogate recovery, where applicable; (6) checks on reagent purity, where applicable; and (7) checks on glassware cleanliness, where applicable.

Calibration Records & Traceability of Standards/Reagents -- Calibration is a reproducible reference point to which all sample measurements can be correlated. A sound calibration program should include provisions for documenting frequency, conditions, standards, and records reflecting the calibration history of a measurement system. The accuracy of the calibration standards is important because all data will be in reference to the standards used. A program for verifying and documenting the accuracy and traceability of all working standards against appropriate primary grade standards or the highest quality standards available should be routinely followed.

Sample Management -- All required records pertaining to sample management should be maintained and updated regularly. These include chain-of-custody forms, sample receipt forms, and sample disposition records.

Original Data -- The raw data and calculated results for all samples should be maintained in laboratory notebooks, logs, benchsheets, files or other sample tracking or data entry forms. Instrumental output should be stored in a computer file or a hardcopy report.

QC Data -- The raw data and calculated results for all QC and field samples and standards should be maintained in the manner described in the preceding paragraph. Documentation should allow correlation of sample results with associated QC data. Documentation should also include the source and lot numbers of standards for traceability. QC samples include, but are not limited to, control samples, method blanks, matrix spikes, and matrix spike duplicates.

Correspondence -- Project correspondence can provide evidence supporting technical interpretations. Correspondence pertinent to the project should be kept and placed in the project files.

Deviations -- All deviations from procedural and planning documents should be recorded in laboratory notebooks. Deviations from QAPjPs should be reviewed and approved by the authorized personnel who performed the original technical review or by their designees.

Final Report -- A copy of any report issued and any supporting documentation should be retained.

5.0 DEFINITIONS

The following terms are defined for use in this document:

ACCURACY — The closeness of agreement between an observed value and an accepted reference value. When applied to a set of observed values, accuracy will be a combination of a random component and of a common systematic error (or bias) component.

BATCH: — A group of samples which behave similarly with respect to the sampling or the testing procedures being employed and which are processed as a unit (see Section 3.4.1 for field samples and Section 4.4.3 for laboratory samples). For QC purposes, if the number of samples in a group is greater than 20, then each group of 20 samples or less will all be handled as a separate batch.

BIAS: — The deviation due to matrix effects of the measured value ($x_s - x_u$) from a known spiked amount. Bias can be assessed by comparing a measured value to an accepted reference value in a sample of known concentration or by determining the recovery of a known amount of contaminant spiked into a sample (matrix spike). Thus, the bias (B) due to matrix effects based on a matrix spike is calculated as:

$$B = (x_s - x_u) - K$$

where:

x_s = measured value for spiked sample,
x_u = measured value for unspiked sample, and
K = known value of the spike in the sample.

Using the following equation yields the percent recovery (%R).

$$\%R = 100\ (x_s - x_u)/\ K$$

BLANK: see Equipment Rinsate, Method Blank, Trip Blank.

CONTROL SAMPLE: A QC sample introduced into a process to monitor the performance of the system.

DATA QUALITY OBJECTIVES (DQOs): A statement of the overall level of uncertainty that a decision-maker is willing to accept in results derived from environmental data (see reference 2, EPA/QAMS, July 16, 1986). This is qualitatively distinct from quality measurements such as precision, bias, and detection limit.

DATA VALIDATION: The process of evaluating the available data against the project DQOs to make sure that the objectives are met. Data validation may be very rigorous, or cursory, depending on project DQOs. The available data reviewed will include analytical results, field QC data and lab QC data, and may also include field records.

DUPLICATE: see Matrix Duplicate, Field Duplicate, Matrix Spike Duplicate.

EQUIPMENT BLANK: see Equipment Rinsate.

EQUIPMENT RINSATE: A sample of analyte-free media which has been used to rinse the sampling equipment. It is collected after completion of decontamination and prior to sampling. This blank is useful in documenting adequate decontamination of sampling equipment.

ESTIMATED QUANTITATION LIMIT (EQL): The lowest concentration that can be reliably achieved within specified limits of precision and accuracy during routine laboratory operating conditions. The EQL is generally 5 to 10 times the MDL. However, it may be nominally chosen within these guidelines to simplify data reporting. For many analytes the EQL analyte concentration is selected as the lowest non-zero standard in the calibration curve. Sample EQLs are highly matrix-dependent. The EQLs in SW-846 are provided for guidance and may not always be achievable.

FIELD DUPLICATES: Independent samples which are collected as close as possible to the same point in space and time. They are two separate samples taken from the same source, stored in separate containers, and analyzed independently. These duplicates are useful in documenting the precision of the sampling process.

LABORATORY CONTROL SAMPLE: A known matrix spiked with compound(s) representative of the target analytes. This is used to document laboratory performance.

MATRIX: The component or substrate (e.g., surface water, drinking water) which contains the analyte of interest.

MATRIX DUPLICATE: An intralaboratory split sample which is used to document the precision of a method in a given sample matrix.

MATRIX SPIKE: An aliquot of sample spiked with a known concentration of target analyte(s). The spiking occurs prior to sample preparation and analysis. A matrix spike is used to document the bias of a method in a given sample matrix.

MATRIX SPIKE DUPLICATES: Intralaboratory split samples spiked with identical concentrations of target analyte(s). The spiking occurs prior to sample preparation and analysis. They are used to document the precision and bias of a method in a given sample matrix.

METHOD BLANK: An analyte-free matrix to which all reagents are added in the same volumes or proportions as used in sample processing. The method blank should be carried through the complete sample preparation and analytical procedure. The method blank is used to document contamination resulting from the analytical process.

For a method blank to be acceptable for use with the accompanying samples, the concentration in the blank of any analyte of concern should not be higher than the highest of either:

(1)The method detection limit, or

(2)Five percent of the regulatory limit for that analyte, or

(3)Five percent of the measured concentration in the sample.

METHOD DETECTION LIMIT (MDL): The minimum concentration of a substance that can be measured and reported with 99% confidence that the analyte concentration is greater than zero and is determined from

analysis of a sample in a given matrix type containing the analyte.

For operational purposes, when it is necessary to determine the MDL in the matrix, the MDL should be determined by multiplying the appropriate one-sided 99% t-statistic by the standard deviation obtained from a minimum of three analyses of a matrix spike containing the analyte of interest at a concentration three to five times the estimated MDL, where the t-statistic is obtained from standard references or the table below.

No. of samples:	t-statistic
3	6.96
4	4.54
5	3.75
6	3.36
7	3.14
8	3.00
9	2.90
10	2.82

Estimate the MDL as follows:
Obtain the concentration value that corresponds to:

a) an instrument signal/noise ratio within the range of 2.5 to 5.0, or

b) the region of the standard curve where there is a significant change in sensitivity (i.e., a break in the slope of the standard curve).

Determine the variance (S^2) for each analyte as follows:

$$s^2 = \frac{1}{n-1}\left[\sum_{i=1}^{n} (x_i - \bar{x})^2\right]$$

where x_i = the ith measurement of the variable x
and $\bar{x}$ = the average value of x;

$$\bar{x} = \frac{1}{n}\sum_{i=1}^{n} x_i$$

Determine the standard deviation (s) for each analyte as follows:

$$s = (S^2)^{1/2}$$

Determine the MDL for each analyte as follows:

$$MDL = t_{(n-1,\ \alpha = .99)}(s)$$

where $t_{(n-1,\ \alpha = .99)}$ is the one-sided t-statistic appropriate for the number of samples used to determine (s), at the 99 percent level.

ORGANIC-FREE REAGENT WATER:

For volatiles, all references to water in the methods refer to water in which an interferant is not observed at the method detection limit of the compounds of interest. Organic-free reagent water can be generated by passing tap water through a carbon filter bed containing about 1 pound of activated carbon. A water purification system may be used to generate organic-free deionized water. Organic-free reagent water may also be prepared by boiling water for 15 minutes and, subsequently, while maintaining the temperature at 90°C, bubbling a contaminant-free inert gas through the water for 1 hour.

For semivolatiles and nonvolatiles, all references to water in the methods refer to water in which an interferant is not observed at the method detection limit of the compounds of interest. Organic-free reagent water can be generated by passing tap water through a carbon filter bed containing about 1 pound of activated carbon. A water purification system may be used to generate organic-free deionized water.

PRECISION:

The agreement among a set of replicate measurements without assumption of knowledge of the true value. Precision is estimated by means of duplicate/replicate analyses. These samples should contain concentrations of analyte above the MDL, and may involve the use of matrix spikes. The most commonly used estimates of precision are the relative standard deviation (RSD) or the coefficient of variation (CV),

$$RSD = CV = 100\ S/\bar{x},$$

where:
$\bar{x}$ = the arithmetic mean of the x_i measurements, and S = variance; and the relative percent difference (RPD) when only two samples are available.

$$RPD = 100\ [(x_1 - x_2)/\{(x_1 + x_2)/2\}].$$

PROJECT: Single or multiple data collection activities that are related through the same planning sequence.

QUALITY ASSURANCE PROJECT PLAN (QAPjP): An orderly assemblage of detailed procedures designed to produce data of sufficient quality to meet the data quality objectives for a specific data collection activity.

RCRA: The Resource Conservation and Recovery Act.

REAGENT BLANK: See Method Blank.

REAGENT GRADE: Analytical reagent (AR) grade, ACS reagent grade, and reagent grade are synonymous terms for reagents which conform to the current specifications of the Committee on Analytical Reagents of the American Chemical Society.

REAGENT WATER: Water that has been generated by any method which would achieve the performance specifications for ASTM Type II water. For organic analyses, see the definition of organic-free reagent water.

REFERENCE MATERIAL: A material containing known quantities of target analytes in solution or in a homogeneous matrix. It is used to document the bias of the analytical process.

SPLIT SAMPLES: Aliquots of sample taken from the same container and analyzed independently. In cases where aliquots of samples are impossible to obtain, field duplicate samples should be taken for the matrix duplicate analysis. These are usually taken after mixing or compositing and are used to document intra- or interlaboratory precision.

STANDARD ADDITION: The practice of adding a known amount of an analyte to a sample immediately prior to analysis. It is typically used to evaluate interferences.

STANDARD CURVE: A plot of concentrations of known analyte standards versus the instrument response to the analyte. Calibration standards are prepared by successively diluting a standard solution to produce working standards which cover the working range of the instrument. Standards should be prepared at the frequency specified in the appropriate

section. The calibration standards should be prepared using the same type of acid or solvent and at the same concentration as will result in the samples following sample preparation. This is applicable to organic and inorganic chemical analyses.

SURROGATE: An organic compound which is similar to the target analyte(s) in chemical composition and behavior in the analytical process, but which is not normally found in environmental samples.

TRIP BLANK: A sample of analyte-free media taken from the laboratory to the sampling site and returned to the laboratory unopened. A trip blank is used to document contamination attributable to shipping and field handling procedures. This type of blank is useful in documenting contamination of volatile organics samples.

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* Definition of term.

CHAPTER TWO

CHOOSING THE CORRECT PROCEDURE

2.1 PURPOSE

This chapter aids the analyst in choosing the appropriate methods for samples, based upon sample matrix and the analytes to be determined.

2.1.1 Trace Analysis vs. Macroanalysis

The methods presented in SW-846 were designed through sample sizing and concentration procedures to address the problem of "trace" analyses (<1000 ppm), and have been developed for an optimized working range. These methods are also applicable to "minor" (1000 ppm - 10,000 ppm) and "major" (>10,000 ppm) analyses, as well as to "trace" analyses, through use of appropriate sample preparation techniques that result in analyte concentration within that optimized range. Such sample preparation techniques include:

1) adjustment of size of sample prepared for analysis,
2) adjustment of injection volumes,
3) dilution or concentration of sample,
4) elimination of concentration steps prescribed for "trace" analyses,
5) direct injection (of samples to be analyzed for volatile constituents).

The performance data presented in each of these methods were generated from "trace" analyses, and may not be applicable to "minor" and "major" analyses. Generally, extraction efficiency improves as concentration increases.

CAUTION: Care should be taken when analyzing samples for trace analyses subsequent to analysis of concentrated samples due to the possibility of contamination.

2.1.2 Choice of Apparatus and Preparation of Reagents

Since many types and sizes of glassware and supplies are commercially available, and since it is possible to prepare reagents and standards in many different ways, those specified in these methods may be replaced by any similar types as long as this substitution does not affect the overall quality of the analyses.

2.2 REQUIRED INFORMATION

In order to choose the correct combination of methods to form the appropriate analytical procedure, some basic information is required.

2.2.1 Physical State(s) of Sample

The phase characteristics of the sample must be known. There are several general categories of phases in which the sample may be categorized:

Aqueous	Oil and Organic Liquid
Sludges	Solids
Multiphase Samples	EP and TCLP Extracts
Ground Water	

2.2.2 Analytes

Analytes are divided into classes based on the determinative methods which are used to identify and quantify them. Table 2-1 lists the organic analytes of SW-846 methods, Table 2-2 lists the analytes that may be prepared using Method 3650, and Table 2-3 lists the analytes that are collected from stack gas effluents using VOST methodology. Tables 2-4 through 2-31 list the target analytes of each organic determinative method. Some of the analytes appear on more than one table, as they may be determined using any of several methods. Table 2-32 indicates which methods are applicable to inorganic target analytes.

2.2.3 Detection Limits Required

Regulations may require a specific sensitivity or detection limit for an analysis, as in the determination of analytes for the Toxicity Characteristic (TC) or for delisting petitions. Drinking water detection limits, for those specific organic and metallic analytes covered by the National Interim Primary Drinking Water Standards, are desired in the analysis of ground water.

2.2.4 Analytical Objective

Knowledge of the analytical objective will be useful in the choice of aliquoting procedures and in the selection of a determinative method. This is especially true when the sample has more than one phase. Knowledge of the analytical objective may not be possible or desirable at all management levels, but that information should be transmitted to the analytical laboratory management to ensure that the correct techniques are being applied to the analytical effort.

2.2.5 Detection and Monitoring

The strategy for detection of compounds in environmental or process samples may be contrasted with the strategy for monitoring samples. Detection samples define initial conditions. When there is little information available about the composition of the sample source, e.g., a well or process stream, mass spectral identification of organic analytes leads to fewer false positive results. Thus, the most practical form of detection for organic analytes, given the analytical requirements, is mass spectral identification. The choice of technique for metals is governed by the detection limit requirements and potential interferents.

Monitoring samples, on the other hand, are analyzed to confirm existing and on-going conditions, tracking the presence or absence of constituents in an

environmental or process matrix. In well defined and stable analytical conditions and matrices less compound-specific detection modes may be used.

2.2.6 Sample Containers, Preservations, and Holding Times

Appropriate sample containers, sample preservation techniques, and sample holding times for aqueous matrices are listed in Table 2-33, near the end of this chapter. Similar information may be found in Table 3-1 of Chapter Three (inorganic analytes) and Table 4-1 of Chapter Four (organic analytes). Samples must be extracted/analyzed within the specified holding times for the results to be considered reflective of total concentrations. Analytical data generated outside of the specified holding times must be considered to be minimum values only. Such data may be used to demonstrate that a waste is hazardous where it shows the concentration of a constituent to be above the regulatory threshold but cannot be used to demonstrate that a waste is not hazardous.

2.3 IMPLEMENTING THE GUIDANCE

The choice of the appropriate sequence of methods depends on the information required and on the experience of the analyst. Figure 2-1 summarizes the organic analysis options available. Appropriate selection is confirmed by the quality control results. The use of the recommended procedures, whether they are approved or mandatory, does not release the analyst from demonstrating the correct execution of the method.

2.3.1 Extraction and Sample Preparation Procedures

Methods for preparing organic analytes are shown in Table 2-34. Method 3500 and associated methods should be consulted for further details on preparing the sample for analysis.

2.3.1.1 Aqueous Samples

The choice of a preparative method depends on the sample. Methods 3510 and 3520 may be used for extraction of the semivolatile organic compounds. Method 3510, a separatory funnel extraction, is appropriate for samples which will not form a persistent emulsion interphase between the sample and the extraction solvent. The formation of an emulsion that cannot be broken up by mechanical techniques will prevent proper extraction of the sample. Method 3520, a liquid-liquid continuous extraction, may be used for any aqueous sample; this method will minimize emulsion formation.

2.3.1.1.1 Basic or Neutral Extraction of Semivolatiles

The solvent extract obtained by performing either Method 3510 or 3520 at a neutral or basic pH will contain the compounds of interest. Refer to Table 1 in the extraction methods (3510 and/or 3520) for guidance on the pH requirements for extraction prior to analysis.

2.3.1.1.2 Acidic Extraction of Phenols and Acids

The extract obtained by performing either Method 3510 or 3520 at a pH less than or equal to 2 will contain the phenols and acid extractables.

2.3.1.2 Solid Samples

Soxhlet (Methods 3540 and 3541) and ultrasonic (Method 3550) extractions are used with solid samples. Consolidated samples should be ground finely enough to pass through a 1 mm sieve. In limited applications, waste dilution (Method 3580) may be used if the entire sample is soluble in the specified solvent.

Methods 3540 and 3541 and 3550 are neutral-pH extraction techniques and therefore, depending on the analysis requirements, acid-base partition cleanup (Method 3650) may be necessary. Method 3650 will only be needed if chromatographic interferences are severe enough to prevent detection of the analytes of interest. This separation will be most important if a GC method is chosen for analysis of the sample. If GC/MS is used, the ion selectivity of the technique may compensate for chromatographic interferences.

2.3.1.3 Oils and Organic Liquids

Method 3580, waste dilution, may be used and the resultant sample analyzed directly by GC or GC/MS. To avoid overloading the analytical detection system, care must be exercised to ensure that proper dilutions are made. Method 3580 gives guidance on performing waste dilutions.

To remove interferences, Method 3611 may be performed on an oil sample directly, without prior sample preparation.

Method 3650 is the only other preparative procedure for oils and other organic liquids. This procedure is a back extraction into an aqueous phase. It is generally introduced as a cleanup procedure for extracts rather than as a preparative procedure. Oils generally have a high concentration of semivolatile compounds and, therefore, preparation by Method 3650 should be done on a relatively small aliquot of the sample. Generally, extraction of 1 mL of oil will be sufficient to obtain a saturated aqueous phase and avoid emulsions.

2.3.1.4 Sludge Samples

There is no set ratio of liquid to solid which enables the analyst to determine which of the three extraction methods cited is the most appropriate. If the sludge is an organic sludge (solid material and organic liquid, as opposed to an aqueous sludge), the sample should be handled as a multiphase sample.

Determining the appropriate methods for analysis of sludges is complicated because of the lack of precise definition of sludges with respect to the relative percent of liquid and solid components. They may be classified into three categories but with appreciable overlap.

2.3.1.4.1 Liquids

Use of Method 3510 or Method 3520 may be applicable to sludges that behave like and have the consistency of aqueous liquids. Ultrasonic extraction (Method 3550) and Soxhlet (Method 3540) procedures will, most likely, be ineffective because of the overwhelming presence of the liquid aqueous phase.

2.3.1.4.2 Solids

Soxhlet (Methods 3540 and 3541) and ultrasonic extraction (Method 3550) will be more effective when applied to sludge samples that resemble solids. Samples may be dried or centrifuged to form solid materials for subsequent determination of semivolatile compounds.

Using Method 3650, Acid-Base Partition Cleanup, on the extract may be necessary, depending on whether chromatographic interferences prevent determination of the analytes of interest.

2.3.1.4.3 Emulsions

Attempts should be made to break up and separate the phases of an emulsion. Several techniques are effective in breaking emulsions or separating the phases of emulsions.

1. Freezing/thawing: Certain emulsions will separate if exposed to temperatures below 0°C.

2. Salting out: Addition of a salt to make the aqueous phase of an emulsion too polar to support a less polar phase promotes separation.

3. Centrifugation: Centrifugal force may separate emulsion components by density.

4. Addition of water or ethanol: Emulsion polymers may be destabilized when a preponderance of the aqueous phase is added.

If techniques for breaking emulsions fail, use Method 3520. If the emulsion can be broken, the different phases (aqueous, solid, or organic liquid) may then be analyzed separately.

2.3.1.5 Multiphase Samples

Choice of the procedure for aliquoting multiphase samples is very dependent on the objective of the analysis. With a sample in which some of the phases tend to separate rapidly, the percent weight or volume of each phase should be calculated and each phase should be individually analyzed for the required analytes.

An alternate approach is to obtain a homogeneous sample and attempt a single analysis on the combination of phases. This approach will give

no information on the abundance of the analytes in the individual phases other than what can be implied by solubility.

A third alternative is to select phases of interest and to analyze only those selected phases. This tactic must be consistent with the sampling/analysis objectives or it will yield insufficient information for the time and resources expended. The phases selected should be compared with Figure 2-1 and Tables 2-34 through 2-36 for further guidance.

2.3.2 Cleanup Procedures

Each category in Table 2-35, Cleanup of Organic Analyte Extracts, corresponds to one of the possible determinative methods available in the manual. Cleanups employed are determined by the analytes of interest within the extract. However, the necessity of performing cleanup may also depend upon the matrix from which the extract was developed. Cleanup of a sample may be done exactly as instructed in the cleanup method for some of the analytes. There are some instances when cleanup using one of the methods may only proceed after the procedure is modified to optimize recovery and separation. Several cleanup techniques may be possible for each analyte category. The information provided is not meant to imply that any or all of these methods must be used for the analysis to be acceptable. Extracts with components which interfere with spectral or chromatographic determinations are expected to be subjected to cleanup procedures.

The analyst's discretion must determine the necessity for cleanup procedures, as there are no clear cut criteria for indicating their use. Method 3600 and associated methods should be consulted for further details on extract cleanup.

2.3.3 Determinative Procedures

The determinative methods for organic analytes have been divided into three categories, shown in Table 2-36: gas chromatography/mass spectrometry (GC/MS); specific detection methods, i.e., gas chromatography (GC); and high performance liquid chromatography (HPLC). This division is intended to help an analyst choose which determinative method will apply. Under each analyte column, SW-846 method numbers have been indicated, if appropriate, for the determination of the analyte. A blank has been left if no chromatographic determinative method is available.

Generally, the MS procedures are more specific but less sensitive than the appropriate gas chromatographic/specific detection method.

Method 8000 gives a general description of the technique of gas chromatography. This method should be consulted prior to application of any of the gas chromatographic methods.

Methods 8080 and 8081, for organochlorine pesticides and polychlorinated biphenyls, Methods 8140 and 8141, for organophosphorus pesticides, and Methods 8150 and 8151, for chlorinated herbicides, are preferred over GC/MS because of the combination of selectivity and sensitivity of the flame photometric, nitrogen-phosphorus, and electron capture detectors.

Methods 8240 and 8260 are both GC/MS methods for volatile analytes. Method 8240 uses a packed column whereas Method 8260 employs a capillary column. Better chromatographic separation of the volatile compounds may be obtained by using Method 8260 rather than 8240. Performance criteria will be based on Method 8260. Method 5030 has been combined with both Method 8240 and 8260, with which it was used exclusively. A GC with a selective detector is also useful for the determination of volatile organic compounds in a monitoring scenario, described in Sec. 2.2.5.

Methods 8250 and 8270 are both GC/MS methods for semivolatile analytes. Method 8250 uses a packed column whereas Method 8270 employs a capillary column. Better chromatographic separation of the semivolatile compounds may be obtained by using Method 8270 rather than 8250. Performance criteria will be based on Method 8270.

2.4 CHARACTERISTICS

Figure 2-2 outlines a sequence for determining if a waste exhibits one or more of the characteristics of a hazardous waste.

2.4.1 EP and TCLP extracts

The leachate obtained from using either the EP (Figure 2-3A) or the TCLP (Figure 2-3B) is an aqueous sample, and therefore, requires further solvent extraction prior to the analysis of semivolatile compounds.

The TCLP leachate is solvent extracted with methylene chloride at a pH > 11 and at a pH <2 by either Method 3510 or 3520. Method 3510 should be used unless the formation of emulsions between the sample and the solvent prevent proper extraction. If this problem is encountered, Method 3520 should be employed.

The solvent extract obtained by performing either Method 3510 or 3520 at a basic or neutral pH will contain the base/neutral compounds of interest. Refer to the specific determinative method for guidance on the pH requirements for extraction prior to analysis.

Due to the high concentration of acetate in the TCLP extract, it is recommended that purge-and-trap be used to introduce the volatile sample into the gas chromatograph.

2.5 GROUND WATER

Appropriate analysis schemes for the determination of analytes in ground water are presented in Figures 2-4A, 2-4B, and 2-4C. Quantitation limits for the metallic analytes should correspond to the drinking water limits which are available.

2.5.1 Special Techniques for Metal Analytes

All atomic absorption analyses should employ appropriate background correction systems whenever spectral interferences could be present. Several background correction techniques are employed in modern atomic absorption spectrometers. Matrix modification can complement background correction in some cases. Since no approach to interference correction is completely effective in all cases, the analyst should attempt to verify the adequacy of correction. If the interferant is known (e.g. high concentrations of iron in the determination of selenium), accurate analyses of synthetic solutions of the interferant (with and without analyte) could establish the efficacy of the background correction. If the nature of the interferant is not established, good agreement of analytical results using two substantially different wavelengths could substantiate the adequacy of the background correction.

To reduce matrix interferences, all graphite furnace atomic absorption (GFAA) analyses should be performed using techniques which maximize an isothermal environment within the furnace cell. Data indicate that two such techniques, L'vov platform and the Delayed Atomization Cuvette (DAC), are equivalent in this respect, and produce high quality results.

All furnace atomic absorption analysis should be carried out using the best matrix modifier for the analysis. Some examples of modifiers are listed below. (See also the appropriate methods.)

Element(s)	Modifier(s)
As and Se	Nickel nitrate, palladium
Pb	Phosphoric acid, ammonium phosphate, palladium
Cd	Ammonium phosphate, palladium
Sb	Ammonium nitrate, palladium
Tl	Platinum, palladium

The ICP calibration standards must match the acid composition and strength of the acids contained in the samples. Acid strengths in the ICP calibration standards should be stated in the raw data.

2.5.2 Special Techniques for Indicated Analytes and Anions

If an Auto-Analyzer is used to read the cyanide distillates, the spectrophotometer must be used with a 50 mm path length cell. If a sample is found to contain cyanide, the sample must be redistilled a second time and analyzed to confirm the presence of the cyanide. The second distillation must fall within the 14-day holding time.

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TABLE 2-1
DETERMINATIVE ANALYTICAL METHODS FOR ORGANIC COMPOUNDS

Compound	Applicable Method(s)
Acenaphthene	8100, 8250/8270, 8310, 8410
Acenaphthylene	8100, 8250/8270, 8310, 8410
Acetaldehyde	8315
Acetone	8240/8260, 8315
Acetonitrile	8240/8260
Acetophenone	8250/8270
2-Acetylaminofluorene	8270
1-Acetyl-2-thiourea	8270
Acifluorfen	8151
Acrolein (Propenal)	8030/8031, 8240/8260, 8315, 8316
Acrylamide	8032, 8316
Acrylonitrile	8030/8031, 8240/8260, 8316
Alachlor	8081
Aldicarb (Temik)	8318
Aldicarb Sulfone	8318
Aldrin	8080/8081, 8250/8270, 8275
Allyl alcohol	8240/8260
Allyl chloride	8010, 8240/8260
2-Aminoanthraquinone	8270
Aminoazobenzene	8270
4-Aminobiphenyl	8250/8270
2-Amino-4,6-dinitrotoluene (2-Am-DNT)	8330
4-Amino-2,6-dinitrotoluene (4-Am-DNT)	8330
3-Amino-9-ethylcarbazole	8270
Anilazine	8270
Aniline	8250/8270
o-Anisidine	8270
Anthracene	8100, 8250/8270, 8310, 8410
Aramite	8270
Aroclor-1016 (PCB-1016)	8080/8081, 8250/8270
Aroclor-1221 (PCB-1221)	8080/8081, 8250/8270
Aroclor-1232 (PCB-1232)	8080/8081, 8250/8270
Aroclor-1242 (PCB-1242)	8080/8081, 8250/8270
Aroclor-1248 (PCB-1248)	8080/8081, 8250/8270
Aroclor-1254 (PCB-1254)	8080/8081, 8250/8270
Aroclor-1260 (PCB-1260)	8080/8081, 8250/8270
Aspon	8141
Asulam	8321
Atrazine	8141
Azinphos-ethyl	8141
Azinphos-methyl	8140/8141, 8270
Barban	8270
Bentazon	8151

TABLE 2-1.
(Continued)

Compound	Applicable Method(s)
Benzal chloride	8121
Benzaldehyde	8315
Benz(a)anthracene	8100, 8250/8270, 8310, 8410
Benzene	8020, 8021, 8240/8260
Benzidine	8250/8270
Benzo(b)fluoranthene	8100, 8250/8270, 8310
Benzo(j)fluoranthene	8100
Benzo(k)fluoranthene	8100, 8250/8270, 8275, 8310
Benzoic acid	8250/8270, 8410
Benzo(g,h,i)perylene	8100, 8250/8270, 8310
Benzo(a)pyrene	8100, 8250/8270, 8275, 8310, 8410
p-Benzoquinone	8270
Benzotrichloride	8121
Benzyl alcohol	8250/8270
Benzyl benzoate	8061
Benzyl chloride	8010, 8121, 8240/8260
BHC (Hexachlorocyclohexane)	8120
α-BHC (alpha-Hexachlorocyclohexane)	8080/8081, 8121, 8250/8270
β-BHC (beta-Hexachlorocyclohexane)	8080/8081, 8121, 8250/8270
δ-BHC (delta-Hexachlorocyclohexane)	8080/8081, 8121, 8250/8270
γ-BHC (Lindane, gamma-Hexachlorocyclohexane)	8080/8081, 8121, 8250/8270
Bis(2-Chloroethoxy)methane	8010, 8110, 8250/8270, 8410
Bis(2-Chloroethyl)ether	8110, 8250/8270, 8410
Bis(2-Chloroethyl)sulfide	8240/8260
Bis(2-Chloroisopropyl) ether	8010, 8110, 8250/8270, 8410
Bis(2-Ethylhexyl) phthalate	8060/8061, 8250/8270, 8410
Bolstar (Sulprofos)	8140/8141
Bromoacetone	8010, 8240/8260
Bromobenzene	8010, 8021, 8260
Bromochloromethane	8021, 8240/8260
Bromodichloromethane	8010, 8021, 8240/8260
4-Bromofluorobenzene	8240/8260
Bromoform	8010, 8021, 8240/8260
Bromomethane	8010, 8021, 8240/8260
4-Bromophenyl phenyl ether	8110, 8250/8270, 8410
Bromoxynil	8270
Butanal	8315
n-Butanol	8260
2-Butanone (Methyl ethyl ketone, MEK)	8015, 8240/8260
n-Butylbenzene	8021, 8260
sec-Butylbenzene	8021, 8260
tert-Butylbenzene	8021, 8260
Butyl benzyl phthalate	8060/8061, 8250/8270, 8410

TABLE 2-1.
(Continued)

Compound	Applicable Method(s)
2-sec-Butyl-4,6-dinitrophenol (DNBP, Dinoseb)	8040, 8150/8151, 8270, 8321
Captafol	8081, 8270
Captan	8081, 8270
Carbaryl (Sevin)	8270, 8318
Carbazole	8275
Carbofuran (Furaden)	8270, 8318
Carbon disulfide	8240/8260
Carbon tetrachloride	8010, 8021, 8240/8260
Carbophenothion (Carbofenthion)	8141, 8270
Chloral hydrate	8240/8260
Chloramben	8151
Chlordane (technical)	8080, 8250/8270
α-Chlordane	8081
γ-Chlordane	8081
Chlorfenvinphos	8141, 8270
Chloroacetonitrile	8260
4-Chloroaniline	8250/8270, 8410
Chlorobenzene	8010, 8020, 8021, 8240/8260
Chlorobenzilate	8081, 8270
2-Chloro-1,3-butadiene	8260
1-Chlorobutane	8260
Chlorodibromomethane (Dibromochloromethane)	8010, 8021, 8240/8260
Chloroethane	8010, 8021, 8240/8260
2-Chloroethanol	8010, 8240/8260
2-Chloroethyl vinyl ether	8010, 8240/8260
Chloroform	8010, 8021, 8240/8260
1-Chlorohexane	8010, 8260
Chloromethane	8010, 8021, 8240/8260
5-Chloro-2-methylaniline	8270
Chloromethyl methyl ether	8010
4-Chloro-3-methylphenol	8040, 8250/8270, 8275, 8410
Chloroneb	8081
3-(Chloromethyl)pyridine hydrochloride	8270
1-Chloronaphthalene	8250/8270, 8275
2-Chloronaphthalene	8120/8121, 8250/8270, 8410
2-Chlorophenol	8040, 8250/8270, 8275, 8410
4-Chlorophenol	8410
4-Chloro-1,2-phenylenediamine	8270
4-Chloro-1,3-phenylenediamine	8270
4-Chlorophenyl phenyl ether	8110, 8250/8270, 8410
Chloroprene	8010, 8240/8260
3-Chloropropene	8260
3-Chloropropionitrile	8240/8260
Chloropropylate	8081

TABLE 2-1.
(Continued)

Compound	Applicable Method(s)
Chlorothalonil	8081
2-Chlorotoluene	8021, 8260
4-Chlorotoluene	8010, 8021, 8260
Chlorpyrifos	8140/8141
Chlorpyrifos methyl	8141
Chrysene	8100, 8250/8270, 8310, 8410
Coumaphos	8140/8141, 8270
Coumarin Dyes	8321
p-Cresidine	8270
o-Cresol (2-Methylphenol)	8250/8270, 8410
m-Cresol (3-Methylphenol)	8270
p-Cresol (4-Methylphenol)	8250/8270, 8275, 8410
Cresols (Methylphenols, Cresylic acids)	8040
Crotonaldehyde	8260, 8315
Crotoxyphos	8141, 8270
Cyclohexanone	8315
2-Cyclohexyl-4,6-dinitrophenol	8040, 8270
2,4-D	8150/8151, 8321
Dalapon	8150/8151, 8321
2,4-DB	8150/8151, 8321
DBCP	8081
2,4-D, butoxyethanol ester	8321
DCPA	8081
DCPA diacid	8151
4,4'-DDD	8080/8081, 8250/8270
4,4'-DDE	8080/8081, 8270
4,4'-DDT	8080/8081, 8250/8270
Decanal	8315
Demeton-O, and -S	8140/8141, 8270
2,4-D,ethylhexyl ester	8321
Diallate	8081, 8270
2,4-Diaminotoluene	8270
Diazinon	8140/8141
Dibenz(a,h)acridine	8100
Dibenz(a,j)acridine	8100, 8250/8270
Dibenz(a,h)anthracene	8100, 8250/8270, 8310
7H-Dibenzo(c,g)carbazole	8100
Dibenzofuran	8250/8270, 8410
Dibenzo(a,e)pyrene	8100, 8270
Dibenzo(a,h)pyrene	8100
Dibenzo(a,i)pyrene	8100
Dibenzothiophene	8275
Dibromochloromethane (Chlorodibromomethane)	8010, 8021, 8240/8260
1,2-Dibromo-3-chloropropane	8010, 8011, 8240/8260, 8270

TABLE 2-1.
(Continued)

Compound	Applicable Method(s)
1,2-Dibromoethane (Ethylene dibromide)	8010, 8011, 8021, 8240/8260
Dibromofluoromethane	8260
Dibromomethane	8010, 8021, 8240/8260
Di-n-butyl phthalate	8060/8061, 8250/8270, 8410
Dicamba	8150/8151, 8321
Dichlone	8081, 8270
1,2-Dichlorobenzene	8010, 8020, 8021, 8120/8121, 8250/8270, 8260, 8410
1,3-Dichlorobenzene	8010, 8020, 8021, 8120/8121, 8250/8270, 8260, 8410
1,4-Dichlorobenzene	8010, 8020, 8021, 8120/8121, 8250/8270, 8260, 8410
3,3'-Dichlorobenzidine	8250/8270
3,5-Dichlorobenzoic acid	8151
1,4-Dichloro-2-butene	8010, 8240
cis-1,4-Dichloro-2-butene	8260
trans-1,4-Dichloro-2-butene	8260
Dichlorodifluoromethane	8010, 8021, 8240/8260
1,1-Dichloroethane	8010, 8021, 8240/8260
1,2-Dichloroethane	8010, 8021, 8240/8260
1,1-Dichloroethene (Vinylidene chloride)	8010, 8021, 8240/8260
cis-1,2-Dichloroethene	8021, 8260
trans-1,2-Dichloroethene	8010, 8021, 8240/8260
Dichlorofenthion	8141
Dichloromethane (Methylene chloride)	8010, 8021, 8240/8260
2,4-Dichlorophenol	8040, 8250/8270, 8275, 8410
2,6-Dichlorophenol	8040, 8250/8270
Dichlorprop	8150/8151, 8321
1,2-Dichloropropane	8010, 8021, 8240/8260
1,3-Dichloropropane	8021, 8260
2,2-Dichloropropane	8021, 8260
1,3-Dichloro-2-propanol	8010, 8240/8260
1,1-Dichloropropene	8021, 8260
cis-1,3-Dichloropropene	8010, 8021, 8240/8260
trans-1,3-Dichloropropene	8010, 8021, 8240/8260
Dichlorvos (Dichlorovos)	8140/8141, 8270, 8321
Dichrotophos	8141, 8270
Dicofol	8081
Dieldrin	8080/8081, 8250/8270
1,2,3,4-Diepoxybutane	8240/8260
Diethyl ether	8015, 8260
Diethyl phthalate	8060/8061, 8250/8270, 8410
Diethylstilbestrol	8270
Diethyl sulfate	8270

TABLE 2-1.
(Continued)

Compound	Applicable Method(s)
1,4-Difluorobenzene	8240/8260
Dihydrosaffrole	8270
Dimethoate	8141, 8270, 8321
3,3'-Dimethoxybenzidine	8270
Dimethylaminoazobenzene	8250/8270
2,5-Dimethylbenzaldehyde	8315
7,12-Dimethylbenz(a)anthracene	8250/8270
3,3'-Dimethylbenzidine	8270
α,α-Dimethylphenethylamine	8250/8270
2,4-Dimethylphenol	8040, 8250/8270
Dimethyl phthalate	8060/8061, 8250/8270, 8410
Dinitrobenzene	8090
1,2-Dinitrobenzene	8270
1,3-Dinitrobenzene (1,3-DNB)	8270, 8330
1,4-Dinitrobenzene	8270
4,6-Dinitro-2-methylphenol	8250/8270, 8410
2,4-Dinitrophenol	8040, 8250/8270, 8410
2,4-Dinitrotoluene (2,4-DNT)	8090, 8250/8270, 8275, 8330, 8410
2,6-Dinitrotoluene (2,6-DNT)	8090, 8250/8270, 8330, 8410
Dinocap	8270
Dinoseb (2-sec-Butyl-4,6-dinitrophenol, DNBP)	8040, 8150/8151, 8270, 8321
Di-n-octyl phthalate	8060/8061, 8250/8270, 8410
Di-n-propyl phthalate	8410
Dioxacarb	8318
1,4-Dioxane	8240/8260
Dioxathion	8141, 8270
Diphenylamine	8250/8270, 8275
5,5-Diphenylhydantoin	8270
1,2-Diphenylhydrazine	8250/8270
Disperse Blue 3	8321
Disperse Blue 14	8321
Disperse Brown 1	8321
Disperse Orange 3	8321
Disperse Orange 30	8321
Disperse Red 1	8321
Disperse Red 5	8321
Disperse Red 13	8321
Disperse Red 60	8321
Disperse Yellow 5	8321
Disulfoton	8140/8141, 8270, 8321
Endosulfan I	8080/8081, 8250/8270
Endosulfan II	8080/8081, 8250/8270
Endosulfan sulfate	8080/8081, 8250/8270

TABLE 2-1.
(Continued)

Compound	Applicable Method(s)
Endrin	8080/8081, 8250/8270
Endrin aldehyde	8080/8081, 8250/8270
Endrin ketone	8081, 8250/8270
Epichlorohydrin	8010, 8240/8260
EPN	8141, 8270
Ethanol (Ethyl alcohol)	8015, 8240/8260
Ethion	8141, 8270
Ethoprop	8140/8141
Ethyl acetate	8260
Ethylbenzene	8020, 8021, 8240/8260
Ethyl carbamate	8270
Ethylene dibromide	8010, 8011, 8021, 8240/8260
Ethylene oxide	8240/8260
Ethyl methacrylate	8240/8260
Ethyl methanesulfonate	8250/8270
Ethyl parathion	8270
Etridiazole	8081
Famphur	8141, 8270, 8321
Fenitrothion	8141
Fensulfothion	8140/8141, 8270, 8321
Fenthion	8140/8141, 8270
Fluchloralin	8270
Fluoranthene	8100, 8250/8270, 8310, 8410
Fluorene	8100, 8250/8270, 8275, 8310, 8410
Fluorescent Brightener 61	8321
Fluorescent Brightener 236	8321
Fluorobenzene	8260
2-Fluorobiphenyl	8250/8270
2-Fluorophenol	8250/8270
Fonophos	8141
Formaldehyde	8315
Halowax-1000	8081
Halowax-1001	8081
Halowax-1013	8081
Halowax-1014	8081
Halowax-1051	8081
Halowax-1099	8081
Heptachlor	8080/8081, 8250/8270
Heptachlor epoxide	8080/8081, 8250/8270
Heptanal	8315
Hexachlorobenzene	8081, 8120/8121, 8250/8270, 8275, 8410

TABLE 2-1.
(Continued)

Compound	Applicable Method(s)
Hexachlorobutadiene (1,3-Hexachlorobutadiene)	8021, 8120/8121, 8250/8270, 8260, 8410
Hexachlorocyclohexane	8120
α-Hexachlorocyclohexane (α-BHC)	8080/8081, 8120/8121, 8250, 8270
β-Hexachlorocyclohexane (β-BHC)	8080/8081, 8120/8121, 8250, 8270
δ-Hexachlorocyclohexane (δ-BHC)	8080/8081, 8120/8121, 8250, 8270
γ-Hexachlorocyclohexane (γ-BHC)	8080/8081, 8120/8121, 8250, 8270
Hexachlorocyclopentadiene	8081, 8120/8121, 8250/8270, 8410
Hexachloroethane	8120/8121, 8250/8270, 8260, 8410
Hexachlorophene	8270
Hexachloropropene	8270
Hexahydro-1,3,5-trinitro-1,3,5-triazine (RDX)	8330
Hexamethylphosphoramide (HMPA)	8141, 8270
Hexanal	8315
2-Hexanone	8240/8260
HMX	8330
1,2,3,4,6,7,8-HpCDD	8280/8290
1,2,3,4,6,7,8-HpCDF	8280/8290
1,2,3,4,7,8,9-HpCDF	8280/8290
1,2,3,4,7,8-HxCDD	8280/8290
1,2,3,6,7,8-HxCDD	8280/8290
1,2,3,7,8,9-HxCDD	8280/8290
1,2,3,4,7,8-HxCDF	8280/8290
1,2,3,6,7,8-HxCDF	8280/8290
1,2,3,7,8,9-HxCDF	8280/8290
2,3,4,6,7,8-HxCDF	8280/8290
Hydroquinone	8270
3-Hydroxycarbofuran	8318
5-Hydroxydicamba	8151
2-Hydroxypropionitrile	8240/8260
Indeno(1,2,3-cd)pyrene	8100, 8250/8270, 8310
Iodomethane	8240/8260
Isobutyl alcohol (2-Methyl-1-propanol)	8240/8260
Isodrin	8081, 8270
Isophorone	8090, 8250/8270, 8410
Isopropylbenzene	8021, 8260
p-Isopropyltoluene	8021, 8260
Isosafrole	8270

TABLE 2-1.
(Continued)

Compound	Applicable Method(s)
Isovaleraldehyde	8315
Kepone	8081, 8270
Leptophos	8141, 8270
Malathion	8141, 8270
Maleic anhydride	8270
Malononitrile	8240/8260
MCPA	8150/8151, 8321
MCPP	8150/8151, 8321
Merphos	8140/8141, 8321
Mestranol	8270
Methacrylonitrile	8240/8260
Methanol	8260
Methapyrilene	8270
Methiocarb (Mesurol)	8318
Methomyl (Lannate)	8318, 8321
Methoxychlor (4,4'-Methoxychlor)	8080/8081, 8250/8270
Methyl acrylate	8260
Methyl-t-butyl ether	8260
3-Methylcholanthrene	8100, 8250/8270
2-Methyl-4,6-dinitrophenol	8040
4,4'-Methylenebis(2-chloroaniline)	8270
4,4'-Methylenebis(N,N-dimethylaniline)	8270
Methyl ethyl ketone (MEK, 2-Butanone)	8015, 8240/8260
Methylene chloride (Dichloromethane)	8010, 8021, 8240/8260
Methyl iodide	8010, 8240/8260
Methyl isobutyl ketone (4-Methyl-2-pentanone)	8015, 8240/8260
Methyl methacrylate	8240/8260
Methyl methanesulfonate	8250/8270
2-Methylnaphthalene	8250/8270, 8410
2-Methyl-5-nitroaniline	8270
Methyl parathion	8270, 8321
4-Methyl-2-pentanone (Methyl isobutyl ketone)	8015, 8240/8260
2-Methylphenol (o-Cresol)	8250/8270, 8410
3-Methylphenol (m-Cresol)	8270
4-Methylphenol (p-Cresol)	8250/8270, 8275, 8410
2-Methylpyridine	8270
Methyl-2,4,6-trinitrophenylnitramine (Tetryl)	8330
Mevinphos	8140/8141, 8270
Mexacarbate	8270
Mirex	8081, 8270
Monochrotophos	8141, 8270, 8321
Naled	8140/8141, 8270, 8321
Naphthalene	8021, 8100, 8250/8270, 8260, 8275, 8310, 8410

TABLE 2-1.
(Continued)

Compound	Applicable Method(s)
Naphthoquinone	8090
1,4-Naphthoquinone	8270
1-Naphthylamine	8250/8270
2-Naphthylamine	8250/8270
Nicotine	8270
5-Nitroacenaphthene	8270
2-Nitroaniline	8250/8270, 8410
3-Nitroaniline	8250/8270, 8410
4-Nitroaniline	8250/8270, 8410
5-Nitro-o-anisidine	8270
Nitrobenzene (NB)	8090, 8250/8270, 8260, 8330, 8410
4-Nitrobiphenyl	8270
Nitrofen	8081, 8270
2-Nitrophenol	8040, 8250/8270, 8410
4-Nitrophenol	8040, 8151, 8250/8270, 8410
2-Nitropropane	8260
Nitroquinoline-1-oxide	8270
N-Nitrosodibutylamine	8250/8270
N-Nitrosodiethylamine	8270
N-Nitrosodimethylamine	8070, 8250/8270, 8410
N-Nitrosodiphenylamine	8070, 8250/8270, 8410
N-Nitrosodi-n-propylamine	8070, 8250/8270, 8410
N-Nitrosomethylethylamine	8270
N-Nitrosomorpholine	8270
N-Nitrosopiperidine	8250/8270
N-Nitrosopyrrolidine	8270
o-Nitrotoluene (2-NT)	8330
m-Nitrotoluene (3-NT)	8330
p-Nitrotoluene (4-NT)	8330
5-Nitro-o-toluidine	8270
trans-Nonachlor	8081
Nonanal	8315
OCDD	8280/8290
OCDF	8280/8290
Octahydro-1,3,5,7-tetranitro-1,3,5,7-tetrazocine (HMX)	8330
Octamethyl pyrophosphoramide	8270
Octanal	8315
4,4'-Oxydianiline	8270
Parathion	8270
Parathion, ethyl	8141
Parathion, methyl	8140/8141
PCB-1016 (Aroclor-1016)	8080/8081, 8250/8270

TABLE 2-1.
(Continued)

Compound	Applicable Method(s)
PCB-1221 (Aroclor-1221)	8080/8081, 8250/8270
PCB-1232 (Aroclor-1232)	8080/8081, 8250/8270
PCB-1242 (Aroclor-1242)	8080/8081, 8250/8270
PCB-1248 (Aroclor-1248)	8080/8081, 8250/8270
PCB-1254 (Aroclor-1254)	8080/8081, 8250/8270
PCB-1260 (Aroclor-1260)	8080/8081, 8250/8270
PCNB	8081
1,2,3,4,7-PeCDD	8280/8290
1,2,3,7,8-PeCDD	8280/8290
1,2,3,7,8-PeCDF	8280/8290
2,3,4,7,8-PeCDF	8280/8290
Pentachlorobenzene	8121, 8250/8270
Pentachloroethane	8240/8260
Pentachlorohexane	8120
Pentachloronitrobenzene	8250/8270
Pentachlorophenol	8040, 8151, 8250/8270, 8410
Pentafluorobenzene	8260, 4010
Pentanal	8315
trans-Permethrin	8081
Perthane	8081
Phenacetin	8250/8270
Phenanthrene	8100, 8250/8270, 8275, 8310, 8410
Phenobarbital	8270
Phenol	8040, 8250/8270, 8410
1,4-Phenylenediamine	8270
Phorate	8140/8141, 8270, 8321
Phosalone	8270
Phosmet	8141, 8270
Phosphamidion	8141, 8270
Phthalic anhydride	8270
Picloram	8151
2-Picoline	8240/8260, 8250/8270
Piperonyl sulfoxide	8270
Promecarb	8318
Pronamide	8250/8270
Propachlor	8081
Propanal	8315
Propargyl alcohol	8240/8260
ß-Propiolactone	8240/8260
Propionitrile	8240/8260
Propoxur (Baygon)	8318
n-Propylamine	8240/8260
n-Propylbenzene	8021, 8260

TABLE 2-1.
(Continued)

Compound	Applicable Method(s)
Propylthiouracil	8270
Pyrene	8100, 8250/8270, 8275, 8310, 8410
Pyridine	8240/8260, 8270
RDX	8330
Resorcinol	8270
Ronnel	8140/8141
Safrole	8270
Simazine	8141
Solvent Red 3	8321
Solvent Red 23	8321
Stirophos (Tetrachlorvinphos)	8140/8141, 8270
Strobane	8081
Strychnine	8270, 8321
Styrene	8021, 8240/8260
Sulfallate	8270
Sulfotepp	8141
2,4,5-T	8150/8151, 8321
2,4,5-T, butoxyethanol ester	8321
2,4,5-T, butyl ester	8321
1,2,3,4-TCDD	8280
1,2,7,8-TCDD	8280
1,2,8,9-TCDD	8280
1,3,6,8-TCDD	8280
1,3,7,8-TCDD	8280
1,3,7,9-TCDD	8280
2,3,7,8-TCDD	8280/8290
1,2,7,8-TCDF	8280
2,3,7,8-TCDF	8280/8290
TEPP	8141
Terbuphos (Terbufos)	8141, 8270
Terphenyl	8250/8270
1,2,3,4-Tetrachlorobenzene	8121
1,2,3,5-Tetrachlorobenzene	8121
1,2,4,5-Tetrachlorobenzene	8121, 8250/8270
Tetrachlorobenzenes	8120
1,1,1,2-Tetrachloroethane	8010, 8021, 8240/8260
1,1,2,2-Tetrachloroethane	8010, 8021, 8240/8260
Tetrachloroethene	8010, 8021, 8240/8260
2,3,4,6-Tetrachlorophenol	8250/8270
Tetrachlorophenols	8040
Tetrachlorvinphos (Stirophos)	8140/8141, 8270
Tetraethyl dithiopyrophosphate	8270
Tetraethyl pyrophosphate	8270

TABLE 2-1.
(Continued)

Compound	Applicable Method(s)
Tetrazene	8331
Thiofanox	8321
Thionazine	8141, 8270
Thiophenol (Benzenethiol)	8270
TOCP (Tri-o-cresylphosphate)	8141
Tokuthion (Prothiofos)	8140/8141
m-Tolualdehyde	8315
o-Tolualdehyde	8315
p-Tolualdehyde	8315
Toluene	8020, 8021, 8240/8260
Toluene diisocyanate	8270
o-Toluidine	8270
Toxaphene	8080/8081, 8250/8270
2,4,5-TP (Silvex)	8150/8151, 8321
2,4,6-Tribromophenol	8250/8270
1,2,3-Trichlorobenzene	8021, 8121, 8260
1,2,4-Trichlorobenzene	8021, 8120/8121, 8250/8270, 8260, 8410
1,3,5-Trichlorobenzene	8121
1,1,1-Trichloroethane	8010, 8021, 8240/8260
1,1,2-Trichloroethane	8010, 8021, 8240/8260
Trichloroethene	8010, 8021, 8240/8260
Trichlorofluoromethane	8010, 8021, 8240/8260
Trichlorfon	8141, 8321
Trichloronate	8140/8141
2,4,5-Trichlorophenol	8250/8270, 8410
2,4,6-Trichlorophenol	8040, 8250/8270, 8410
Trichlorophenols	8040
1,2,3-Trichloropropane	8010, 8021, 8240/8260
O,O,O-Triethyl phosphorothioate	8270
Trifluralin	8081, 8270
2,4,5-Trimethylaniline	8270
1,2,4-Trimethylbenzene	8021, 8260
1,3,5-Trimethylbenzene	8021, 8260
Trimethyl phosphate	8270
1,3,5-Trinitrobenzene (1,3,5-TNB)	8270, 8330
2,4,6-Trinitrotoluene (2,4,6-TNT)	8330
Tri-o-cresyl phosphate (TOCP)	8141
Tri-p-tolyl phosphate	8270
Tris(2,3-Dibromopropyl) phosphate (Tris-BP)	8270, 8321
Vinyl acetate	8240/8260
Vinyl chloride	8010, 8021, 8240/8260

TABLE 2-1.
(Continued)

Compound	Applicable Method(s)
o-Xylene	8021, 8260
m-Xylene	8021, 8260
p-Xylene	8021, 8260
Xylene (Total)	8020, 8240

TABLE 2-2A.
METHOD 3650 - BASE/NEUTRAL FRACTION

Benz(a)anthracene
Benzo(a)pyrene
Benzo(b)fluoranthene
Chlordane
Chlorinated dibenzodioxins
Chrysene
Creosote
Dichlorobenzene(s)
Dinitrobenzene
2,4-Dinitrotoluene
Heptachlor
Hexachlorobenzene
Hexachlorobutadiene
Hexachloroethane
Hexachlorocyclopentadiene
Naphthalene
Nitrobenzene
Phorate
2-Picoline
Pyridine
Tetrachlorobenzene(s)
Toxaphene

TABLE 2-2B.
METHOD 3650 - ACID FRACTION

2-Chlorophenol
Cresol(s)
Creosote
Dichlorophenoxyacetic acid
2,4-Dimethylphenol
4,6-Dinitro-o-cresol
4-Nitrophenol
Pentachlorophenol
Phenol
Tetrachlorophenol(s)
Trichlorophenol(s)
2,4,5-TP (Silvex)

TABLE 2-3.
METHOD 5041 - SORBENT CARTRIDGES FROM
VOLATILE ORGANIC SAMPLING TRAIN (VOST)

Acetone
Acrylonitrile
Benzene
Bromodichloromethane
Bromoform[a]
Bromomethane[b]
Carbon disulfide
Carbon tetrachloride
Chlorobenzene
Chlorodibromomethane
Chloroethane[b]
Chloroform
Chloromethane[b]
Dibromomethane
1,1-Dichloroethane
1,2-Dichloroethane
1,1-Dichloroethene
trans-1,2-Dichloroethene
1,2-Dichloropropane
cis-1,3-Dichloropropene
trans-1,3-Dichloropropene
Ethylbenzene[a]
Iodomethane
Methylene chloride
Styrene[a]
1,1,2,2-Tetrachloroethane[a]
Tetrachloroethene
Toluene
1,1,1-Trichloroethane
1,1,2-Trichloroethane
Trichloroethene
Trichlorofluoromethane
1,2,3-Trichloropropane[a]
Vinyl chloride[b]
Xylenes[a]

[a] Boiling point of this compound is above 132°C. Method 0030 is not appropriate for quantitative sampling of this analyte.

[b] Boiling point of this compound is below 30°C. Special precautions must be taken when sampling for this analyte by Method 0030. Refer to Sec. 1.3 of Method 5041 for discussion.

TABLE 2-4.
METHOD 8010 - HALOGENATED VOLATILES

Allyl chloride
Benzyl chloride
Bis(2-chloroethoxy)methane
Bis(2-chloroisopropyl) ether
Bromoacetone
Bromobenzene
Bromodichloromethane
Bromoform
Bromomethane
Carbon tetrachloride
Chlorobenzene
Chloroethane
2-Chloroethanol
2-Chloroethyl vinyl ether
Chloroform
1-Chlorohexane
Chloromethane
Chloromethyl methyl ether
Chloroprene
4-Chlorotoluene
Dibromochloromethane
1,2-Dibromo-3-chloropropane
Dibromomethane
1,2-Dichlorobenzene
1,3-Dichlorobenzene
1,4-Dichlorobenzene
1,4-Dichloro-2-butene
Dichlorodifluoromethane
1,1-Dichloroethane
1,2-Dichloroethane
1,1-Dichloroethene (Vinylidene chloride)
trans-1,2-Dichloroethene
Dichloromethane (Methylene Chloride)
1,2-Dichloropropane
1,3-Dichloro-2-propanol
cis-1,3-Dichloropropene
trans-1,3-Dichloropropene
Epichlorhydrin
Ethylene dibromide
Methyl iodide
1,1,2,2-Tetrachloroethane
1,1,1,2-Tetrachloroethane
Tetrachloroethene
1,1,1-Trichloroethane
1,1,2-Trichloroethane
Trichloroethene
Trichlorofluoromethane
1,2,3-Trichloropropane
Vinyl chloride

For Method 8011, see Table 2-7

TABLE 2-5.
METHOD 8015 - NONHALOGENATED VOLATILES

Diethyl ether
Ethanol
Methyl ethyl ketone (MEK)
Methyl isobutyl ketone (MIBK)

TABLE 2-6.
METHOD 8020 - AROMATIC VOLATILES

Benzene
Chlorobenzene
1,2-Dichlorobenzene
1,3-Dichlorobenzene
1,4-Dichlorobenzene
Ethylbenzene
Toluene
Xylenes

TABLE 2-7.
METHOD 8021 (METHOD 8011*) - HALOGENATED AND AROMATIC VOLATILES

Benzene
Bromobenzene
Bromochloromethane
Bromodichloromethane
Bromoform
Bromomethane
n-Butylbenzene
sec-Butylbenzene
tert-Butylbenzene
Carbon tetrachloride
Chlorobenzene
Chlorodibromomethane
Chloroethane
Chloroform
Chloromethane
2-Chlorotoluene
4-Chlorotoluene
1,2-Dibromo-3-chloropropane*
1,2-Dibromoethane*
Dibromomethane
1,2-Dichlorobenzene
1,3-Dichlorobenzene
1,4-Dichlorobenzene
Dichlorodifluoromethane
1,1-Dichloroethane
1,2-Dichloroethane
1,1-Dichloroethene (Vinylidene chloride)
cis-1,2-Dichloroethene
trans-1,2-Dichloroethene
1,2-Dichloropropane
1,3-Dichloropropane
2,2-Dichloropropane
1,1-Dichloropropene
cis-1,3-Dichloropropene
trans-1,3-Dichloropropene
Ethylbenzene
Hexachlorobutadiene
Isopropylbenzene
p-Isopropyltoluene
Methylene chloride (DCM)
Naphthalene
n-Propylbenzene
Styrene
1,1,1,2-Tetrachloroethane
1,1,2,2-Tetrachloroethane
Tetrachloroethene
Toluene
1,2,3-Trichlorobenzene
1,2,4-Trichlorobenzene
1,1,1-Trichloroethane
1,1,2-Trichloroethane
Trichloroethene
Trichlorofluoromethane
1,2,3-Trichloropropane
1,2,4-Trimethylbenzene
1,3,5-Trimethylbenzene
Vinyl chloride
o-Xylene
m-Xylene
p-Xylene

* Indicates the only two target analytes of Method 8011. These constituents a
also target analytes of Method 8021.

TABLE 2-8.
METHODS 8030/8031 -
ACROLEIN, ACRYLONITRILE

Acrolein (Propenal)*
Acrylonitrile

* Target analyte of Method 8030 only.

TABLE 2-9
METHOD 8032 -
ACRYLAMIDE

Acrylamide

TABLE 2-10.
METHOD 8040 - PHENOLS

2-sec-Butyl-4,6-dinitrophenol (DNBP, Dinoseb)
4-Chloro-3-methylphenol
2-Chlorophenol
Cresols (Methylphenols)
2-Cyclohexyl-4,6-dinitrophenol
2,4-Dichlorophenol
2,6-Dichlorophenol
2,4-Dimethylphenol
2,4-Dinitrophenol
2-Methyl-4,6-dinitrophenol
2-Nitrophenol
4-Nitrophenol
Pentachlorophenol
Phenol
Tetrachlorophenols
2,4,6-Trichlorophenol
Trichlorophenols

TABLE 2-11.
METHODS 8060/8061 - PHTHALATE ESTERS

Benzyl benzoate*
Butyl benzyl phthalate
Bis(2-ethylhexyl) phthalate
Di-n-butyl phthalate
Diethyl phthalate
Dimethyl phthalate
Di-n-octyl phthalate

* Target analyte of Method 8061 only.

TABLE 2-12.
METHOD 8070 - NITROSAMINES

N-Nitrosodimethylamine
N-Nitrosodiphenylamine
N-Nitrosodi-n-propylamine

TABLE 2-13.
METHODS 8080/8081 - ORGANOCHLORINE PESTICIDES AND PCBs

Aroclor-1016 (PCB-1016)
Aroclor-1221 (PCB-1221)
Aroclor-1232 (PCB-1232)
Aroclor-1242 (PCB-1242)
Aroclor-1248 (PCB-1248)
Aroclor-1254 (PCB-1254)
Aroclor-1260 (PCB-1260)
Alachlor*
Aldrin
α-BHC
β-BHC
δ-BHC
γ-BHC (Lindane)
Captafol*
Captan*
Chlorobenzilate*
Chlordane (technical)**
α-Chlordane*
γ-Chlordane*
Chloroneb*
Chloropropylate*
Chlorothalonil*
DBCP*
DCPA*
4,4′-DDD
4,4′-DDE
4,4′-DDT
Diallate*
Dichlone*
Dicofol*
Dieldrin
Endosulfan I
Endosulfan II
Endosulfan sulfate
Endrin
Endrin aldehyde
Endrin ketone*
Etridiazole*
Halowax-1000*
Halowax-1001*
Halowax-1013*
Halowax-1014*
Halowax-1051*
Halowax-1099*
Heptachlor
Heptachlor epoxide
Hexachlorobenzene*
Hexachlorocyclopentadiene*
Isodrin*
Kepone*
Methoxychlor
Mirex*
Nitrofen*
trans-Nonachlor*
PCNB*
trans-Permethrin*
Perthane*
Propachlor*
Strobane*
Toxaphene
Trifluralin*

* Target analyte of Method 8081 only.
** Target analyte of Method 8080 only.

TABLE 2-14.
METHOD 8090 - NITROAROMATICS AND CYCLIC KETONES

Dinitrobenzene
2,4-Dinitrotoluene
2,6-Dinitrotoluene
Isophorone
Naphthoquinone
Nitrobenzene

TABLE 2-15.
METHODS 8100 - POLYNUCLEAR AROMATIC HYDROCARBONS

Acenaphthene
Acenaphthylene
Anthracene
Benzo(a)anthracene
Benzo(b)fluoranthene
Benzo(j)fluoranthene
Benzo(k)fluoranthene
Benzo (g,h,i)perylene
Benzo(a)pyrene
Chrysene
Dibenz(a,h)acridine
Dibenz(a,j)acridine
Dibenzo(a,h)anthracene
7H-Dibenzo(c,g)carbazole
Dibenzo(a,e)pyrene
Dibenzo(a,h)pyrene
Dibenzo(a,i)pyrene
Fluoranthene
Fluorene
Indeno(1,2,3-cd)pyrene
3-Methylcholanthrene
Naphthalene
Phenanthrene
Pyrene

TABLE 2-16
METHOD 8110 - HALOETHERS

Bis(2-Chloroethoxy)methane
Bis(2-Chloroethyl) ether
Bis(2-Chloroisopropyl) ether
4-Bromophenyl phenyl ether
4-Chlorophenyl phenyl ether

TABLE 2-17.
METHODS 8120/8121 - CHLORINATED HYDROCARBONS

Benzal chloride*
Benzotrichloride*
Benzyl chloride*
2-Chloronaphthalene
1,2-Dichlorobenzene
1,3-Dichlorobenzene
1,4-Dichlorobenzene
Hexachlorobenzene
Hexachlorobutadiene
Hexachlorocyclohexane**
α-Hexachlorocyclohexane (α-BHC)*
β-Hexachlorocyclohexane (β-BHC)*
δ-Hexachlorocyclohexane (δ-BHC)*
γ-Hexachlorocyclohexane (γ-BHC)*
Hexachlorocyclopentadiene
Hexachloroethane
Pentachlorobenzene*
Pentachlorohexane**
Tetrachlorobenzenes**
1,2,3,4-Tetrachlorobenzene*
1,2,3,5-Tetrachlorobenzene*
1,2,4,5-Tetrachlorobenzene*
1,2,3-Trichlorobenzene*
1,2,4-Trichlorobenzene
1,3,5-Trichlorobenzene*

* Target analyte of Method 8121 only.
** Target analyte of Method 8120 only.

TABLE 2-18.
METHODS 8140/8141 - ORGANOPHOSPHORUS COMPOUNDS
(PACKED AND CAPILLARY COLUMNS)

Aspon*
Atrazine*
Azinphos ethyl*
Azinphos methyl
Bolstar (Sulprofos)
Carbophenothion*
Chlorofenvinphos*
Chlorpyrifos
Chlorpyrifos methyl*
Coumaphos
Crotoxypos*
Demeton-O, and -S
Diazinon
Dichlorofenthion*
Dichlorvos (DDVP)
Dichrotophos*
Dimethoate*
Dioxathion*
Disulfoton
EPN*
Ethion*
Ethoprop
Famphur*
Fenitrothion*
Fensulfothion
Fenthion
Fonophos*
Hexamethylphosphoramide* (HMPA)
Leptophos*
Malathion*
Merphos
Mevinphos
Monochrotophos*
Naled
Parathion, ethyl*
Parathion, methyl
Phorate
Phosmet*
Phosphamidon*
Ronnel
Simazine*
Stirophos (Tetrachlorvinphos)
Sulfotep*
TEPP*
Terbufos*
Thionazin*
Tokuthion (Prothiofos)
Trichlorfon*
Trichloronate
Tri-o-cresylphosphate (TOCP)*

* Target analyte of Method 8141 only.

TABLE 2-19.
METHODS 8150/8151 - CHLORINATED HERBICIDES

Acifluorfen*
Bentazon*
Chloramben*
2,4-D
Dalapon
2,4-DB
DCPA diacid*
Dicamba
3,5-Dichlorobenzoic acid*
Dichlorprop
Dinoseb (DNBP)
5-Hydroxydicamba*
MCPA
MCPP
4-Nitrophenol*
Pentachlorophenol*
Picloram*
2,4,5-TP (Silvex)
2,4,5-T

* Target analyte of Method 8151 only.

TABLE 2-20.
METHODS 8240/8260 - VOLATILES

Acetone
Acetonitrile
Acrolein (Propenal)
Acrylonitrile
Allyl alcohol
Allyl chloride
Benzene
Benzyl chloride
Bis(2-chloroethyl) sulfide
Bromoacetone
Bromobenzene*
Bromochloromethane
Bromodichloromethane
4-Bromofluorobenzene
Bromoform
Bromomethane
n-Butanol*
2-Butanone (Methyl ethyl ketone)
n-Butylbenzene*
sec-Butylbenzene*
tert-Butylbenzene*
Carbon disulfide
Carbon tetrachloride
Chloral hydrate
Chloroacetonitrile*
Chlorobenzene
2-Chloro-1,3-butadiene*
1-Chlorobutane*
Chlorodibromomethane
Chloroethane
2-Chloroethanol
2-Chloroethyl vinyl ether
Chloroform
1-Chlorohexane*
Chloromethane
Chloroprene
3-Chloropropene*
3-Chloropropionitrile
2-Chlorotoluene*
4-Chlorotoluene*
Crotonaldehyde*
1,2-Dibromo-3-chloropropane
1,2-Dibromoethane
Dibromomethane
Dibromofluoromethane*
1,2-Dichlorobenzene*
1,3-Dichlorobenzene*
1,4-Dichlorobenzene*
1,4-Dichloro-2-butene**
cis-1,4-Dichloro-2-butene*
trans-1,4-Dichloro-2-butene*
1,4-Dichloro-2-butene**
Dichlorodifluoromethane
1,1-Dichloroethane
1,2-Dichloroethane
1,1-Dichloroethene
cis-1,2-Dichloroethene*
trans-1,2-Dichloroethene
1,2-Dichloropropane
1,3-Dichloropropane*
2,2-Dichloropropane*
1,3-Dichloro-2-propanol
1,1-Dichloropropene*
cis-1,3-Dichloropropene
trans-1,3-Dichloropropene
1,2,3,4-Diepoxybutane
Diethyl ether*
1,4-Difluorobenzene
1,4-Dioxane
Epichlorohydrin
Ethanol
Ethyl acetate*
Ethylbenzene
Ethylene oxide
Ethyl methacrylate
Fluorobenzene*
Hexachlorobutadiene*
Hexachloroethane*
2-Hexanone
2-Hydroxypropionitrile
Iodomethane
Isobutyl alcohol
Isopropylbenzene*
p-Isopropyltoluene*
Malononitrile
Methacrylonitrile
Methanol*
Methyl acrylate*
Methyl-t-butyl ether*
Methylene chloride (DCM)
Methyl iodide
Methyl methacrylate
4-Methyl-2-pentanone (MIBK)
Naphthalene*
Nitrobenzene*
2-Nitropropane*
Pentachloroethane
Pentafluorobenzene*
2-Picoline
Propargyl alcohol
β-Propiolactone
Propionitrile
n-Propylamine
n-Propylbenzene*
Pyridine
Styrene
1,1,1,2-Tetrachloroethane
1,1,2,2-Tetrachloroethane
Tetrachloroethene
Toluene
1,2,3-Trichlorobenzene*
1,2,4-Trichlorobenzene*
1,1,1-Trichloroethane
1,1,2-Trichloroethane
Trichloroethene
Trichlorofluoromethane
1,2,3-Trichloropropane
1,2,4-Trimethylbenzene*
1,3,5-Trimethylbenzene*
Vinyl acetate
Vinyl chloride
Xylene (Total)**
o-Xylene*
m-Xylene*
p-Xylene*

* Target analyte of Method 8260 only.
** Target analyte of Method 8240 only.

TABLE 2-21.
METHODS 8250/8270 - SEMIVOLATILES

Acenaphthene
Acenaphthylene
Acetophenone
2-Acetylaminofluorene*
1-Acetyl-2-thiourea*
Aldrin
2-Aminoanthraquinone*
Aminoazobenzene*
4-Aminobiphenyl
3-Amino-9-ethylcarbazole*
Anilazine*
Aniline
o-Anisidine*
Anthracene
Aramite*
Aroclor-1016 (PCB-1016)
Aroclor-1221 (PCB-1221)
Aroclor-1232 (PCB-1232)
Aroclor-1242 (PCB-1242)
Aroclor-1248 (PCB-1248)
Aroclor-1254 (PCB-1254)
Aroclor-1260 (PCB-1268)
Azinphos-methyl*
Barban*
Benz(a)anthracene
Benzidine
Benzo(b)fluoranthene
Benzo(k)fluoranthene
Benzoic acid
Benzo(g,h,i)perylene
Benzo(a)pyrene
p-Benzoquinone*
Benzyl alcohol
α-BHC
β-BHC
δ-BHC
γ-BHC (Lindane)
Bis(2-chloroethoxy)methane
Bis(2-chloroethyl) ether
Bis(2-chloroisopropyl) ether
Bis(2-ethylhexyl) phthalate
4-Bromophenyl phenyl ether
Bromoxynil*
Butyl benzyl phthalate
2-sec-Butyl-4,6-dinitrophenol (Dinoseb)*
Captafol*
Captan*
Carbaryl*
Carbofuran*
Carbophenothion*
Chlordane (technical)
Chlorfenvinphos*
4-Chloroaniline
Chlorobenzilate*
5-Chloro-2-methylaniline*
4-Chloro-3-methylphenol
3-(Chloromethyl)pyridine hydrochloride*
1-Chloronaphthalene
2-Chloronaphthalene
2-Chlorophenol
4-Chloro-1,2-phenylenediamine*
4-Chloro-1,3-phenylenediamine*
4-Chlorophenyl phenyl ether
Chrysene
Coumaphos*
p-Cresidine*
Crotoxyphos*
2-Cyclohexyl-4,6-dinitrophenol*
4,4'-DDD
4,4'-DDE*
4,4'-DDT
Demeton-O*
Demeton-S*
Diallate (cis or trans)*
2,4-Diaminotoluene*
Dibenz(a,j)acridine
Dibenz(a,h)anthracene
Dibenzofuran
Dibenzo(a,e)pyrene*
1,2-Dibromo-3-chloropropane*
Di-n-butyl phthalate
Dichlone*
1,2-Dichlorobenzene
1,3-Dichlorobenzene
1,4-Dichlorobenzene
3,3'-Dichlorobenzidine
2,4-Dichlorophenol
2,6-Dichlorophenol
Dichlorovos*
Dicrotophos*
Dieldrin
Diethyl phthalate
Diethylstilbestrol*
Diethyl sulfate*
Dihydrosaffrole*
Dimethoate*
3,3'-Dimethoxybenzidine*
Dimethylaminoazobenzene

TABLE 2-21.
METHODS 8250/8270 - SEMIVOLATILES (CONTINUED)

7,12-Dimethylbenz(a)anthracene
3,3'-Dimethylbenzidine*
α,α-Dimethylphenethylamine
2,4-Dimethylphenol
Dimethyl phthalate
1,2-Dinitrobenzene*
1,3-Dinitrobenzene*
1,4-Dinitrobenzene*
4,6-Dinitro-2-methylphenol
2,4-Dinitrophenol
2,4-Dinitrotoluene
2,6-Dinitrotoluene
Dinocap*
Dioxathion*
Diphenylamine
5,5-Diphenylhydantoin*
1,2-Diphenylhydrazine
Di-n-octyl phthalate
Disulfoton*
Endosulfan I
Endosulfan II
Endosulfan sulfate
Endrin
Endrin aldehyde
Endrin ketone
EPN*
Ethion*
Ethyl carbamate*
Ethyl methanesulfonate
Ethyl parathion*
Famphur*
Fensulfothion*
Fenthion*
Fluchloralin*
Fluoranthene
Fluorene
2-Fluorobiphenyl
2-Fluorophenol
Heptachlor
Heptachlor epoxide
Hexachlorobenzene
Hexachlorobutadiene
Hexachlorocyclopentadiene
Hexachloroethane
Hexachlorophene*
Hexachloropropene*
Hexamethylphosphoramide*
Hydroquinone*
Indeno(1,2,3-cd)pyrene
Isodrin*
Isophorone
Isosafrole*
Kepone*
Leptophos*
Malathion*
Maleic anhydride*
Mestranol*
Methapyrilene*
Methoxychlor
3-Methylcholanthrene
4,4'-Methylenebis(2-chloroaniline)*
4,4'-Methylenebis(N,N-dimethylaniline)*
Methyl methanesulfonate
2-Methylnaphthalene
2-Methyl-5-nitroaniline*
Methyl parathion*
2-Methylphenol (o-Cresol)
3-Methylphenol (m-Cresol)*
4-Methylphenol (p-Cresol)
2-Methylpyridine*
Mevinphos*
Mexacarbate*
Mirex*
Monocrotophos*
Naled*
Naphthalene
1,4-Naphthoquinone*
1-Naphthylamine
2-Naphthylamine
Nicotine*
5-Nitroacenaphthene*
2-Nitroaniline
3-Nitroaniline
4-Nitroaniline
5-Nitro-o-anisidine*
Nitrobenzene
4-Nitrobiphenyl*
Nitrofen*
2-Nitrophenol
4-Nitrophenol
Nitroquinoline-1-oxide*
N-Nitrosodibutylamine
N-Nitrosodiethylamine*
N-Nitrosodimethylamine
N-Nitrosodiphenylamine
N-Nitrosodi-n-propylamine

TABLE 2-21.
METHODS 8250/8270 - SEMIVOLATILES (CONTINUED)

N-Nitrosomethylethylamine*
N-Nitrosomorpholine*
N-Nitrosopiperidine
N-Nitrosopyrrolidine*
5-Nitro-o-toluidine*
Octamethyl pyrophosphoramide*
4,4'-Oxydianiline*
Parathion*
Pentachlorobenzene
Pentachloronitrobenzene
Pentachlorophenol
Phenacetin
Phenanthrene
Phenobarbital*
Phenol
1,4-Phenylenediamine*
Phorate*
Phosalone*
Phosmet*
Phosphamidion*
Phthalic anhydride*
2-Picoline
Piperonyl sulfoxide*
Pronamide
Propylthiouracil*
Pyrene
Pyridine*
Resorcinol*
Safrole*
Strychnine*
Sulfallate*
Terbuphos*
Terphenyl
1,2,4,5-Tetrachlorobenzene
2,3,4,6-Tetrachlorophenol
Tetrachlorvinphos (Stirophos)*
Tetraethyl dithiopyrophosphate*
Tetraethyl pyrophosphate*
Thionazine*
Thiophenol (Benzenethiol)*
Toluene diisocyanate*
o-Toluidine*
Toxaphene
2,4,6-Tribromophenol
1,2,4-Trichlorobenzene
2,4,5-Trichlorophenol
2,4,6-Trichlorophenol
O,O,O-Triethyl phosphorothioate*
Trifluralin*
2,4,5-Trimethylaniline*
Trimethyl phosphate*
1,3,5-Trinitrobenzene*
Tris(2,3-dibromopropyl) phosphate*
Tri-p-tolyl phosphate*

* Target analyte of Method 8270 only.

TABLE 2-22.
METHOD 8275 - SEMIVOLATILES (SCREENING)

Aldrin
Benzo(k)fluoranthene
Benzo(a)pyrene
Carbazole
4-Chloro-3-methylphenol
1-Chloronaphthalene
2-Chlorophenol
Dibenzothiophene
2,4-Dichlorophenol
2,4-Dinitrotoluene
Diphenylamine
Fluorene
Hexachlorobenzene
4-Methylphenol
Naphthalene
Phenanthrene
Pyrene

TABLE 2-23.
METHODS 8280/8290 - DIOXINS AND DIBENZOFURANS

2,3,7,8-TCDD	1,2,3,4,7-PeCDD	1,2,7,8-TCDF
1,2,3,4-TCDD*	1,2,3,7,8-PeCDD	2,3,7,8-TCDF
1,3,6,8-TCDD*	1,2,3,4,7,8-HxCDD	1,2,3,7,8-PeCDF
1,3,7,9-TCDD*	1,2,3,6,7,8-HxCDD	2,3,4,7,8-PeCDF
1,3,7,8-TCDD*	1,2,3,7,8,9-HxCDD	1,2,3,4,7,8-HxCDF
1,2,7,8-TCDD*	1,2,3,4,6,7,8-HpCDD	1,2,3,6,7,8-HxCDF
1,2,8,9-TCDD*	OCDD	1,2,3,7,8,9-HxCDF
		2,3,4,6,7,8-HxCDF
		1,2,3,4,6,7,8-HpCDF
		1,2,3,4,7,8,9-HpCDF
		OCDF

* Target analyte of 8280 only

TABLE 2-24.
METHOD 8310 - POLYNUCLEAR AROMATIC HYDROCARBONS

Acenaphthene	Chrysene
Acenaphthylene	Dibenzo(a,h)anthracene
Anthracene	Fluoranthene
Benzo(a)anthracene	Fluorene
Benzo(a)pyrene	Indeno(1,2,3-cd)pyrene
Benzo(b)fluoranthene	Naphthalene
Benzo(g,h,i)perylene	Phenanthrene
Benzo(k)fluoranthene	Pyrene

TABLE 2-25.
METHOD 8315 - CARBONYL COMPOUNDS

Acetaldehyde	Heptanal
Acetone	Hexanal (Hexaldehyde)
Acrolein (Propanol)	Isovaleraldehyde
Benzaldehyde	Nonanal
Butanal (Butyraldehyde)	Octanal
Crotonaldehyde	Pentanal (Valeraldehyde)
Cyclohexanone	Propanal (Propionaldehyde)
Decanal	m-Tolualdehyde
2,5-Dimethylbenzaldehyde	o-Tolualdehyde
Formaldehyde	p-Tolualdehyde

TABLE 2-26.
METHOD 8316 - ACRYLAMIDE, ACRYLONITRILE AND ACROLEIN

Acrolein (Propanol)
Acrylamide
Acrylonitrile

TABLE 2-27.
METHOD 8318 - N-METHYLCARBAMATES

Aldicarb (Temik)
Aldicarb Sulfone
Carbaryl (Sevin)
Carbofuran (Furadan)
Dioxacarb
3-Hydroxycarbofuran
Methiocarb (Mesurol)
Methomyl (Lannate)
Promecarb
Propoxur (Baygon)

TABLE 2-28.
METHOD 8321 - NONVOLATILES

Azo Dyes
Disperse Red 1
Disperse Red 5
Disperse Red 13
Disperse Yellow 5
Disperse Orange 3
Disperse Orange 30
Disperse Brown 1
Solvent Red 3
Solvent Red 23

Anthraquinone Dyes
Disperse Blue 3
Disperse Blue 14
Disperse Red 60
Coumarin Dyes

(Fluorescent Brighteners)
Fluorescent Brightener 61
Fluorescent Brightener 236

Chlorinated Phenoxyacid Compounds
2,4-D
2,4-D, butoxyethanol ester
2,4-D, ethylhexyl ester
2,4-DB
Dalapon
Dicamba
Dichlorprop
Dinoseb
MCPA
MCPP
Silvex (2,4,5-TP)
2,4,5-T
2,4,5-T, butyl ester
2,4,5-T, butoxyethanol ester

Alkaloids
Strychnine

Organophosphorus Compounds
Asulam
Dichlorvos
Dimethoate
Disulfoton
Famphur
Fensulfothion
Merphos
Methomyl
Methyl parathion
Monocrotophos
Naled
Phorate
Trichlorfon
Thiofanox
Tris-(2,3-dibromopropyl) phosphate, (Tris-BP)

TABLE 2-29.
METHOD 8330 - NITROAROMATICS AND NITRAMINES

4-Amino-2,6-dinitrotoluene (4-Am-DNT)
2-Amino-4,6-dinitrotoluene (2-Am-DNT)
1,3-Dinitrobenzene (1,3-DNB)
2,4-Dinitrotoluene (2,4-DNT)
2,6-Dinitrotoluene (2,6-DNT)
Hexahydro-1,3,5-trinitro-1,3,5-triazine (RDX)
Methyl-2,4,6-trinitrophenylnitramine (Tetryl)
Nitrobenzene (NB)
2-Nitrotoluene (2-NT)
3-Nitrotoluene (3-NT)
4-Nitrotoluene (4-NT)
Octahydro-1,3,5,7-tetranitro-1,3,5,7-tetrazocine (HMX)
1,3,5-Trinitrobenzene (1,3,5-TNB)
2,4,6-Trinitrotoluene (2,4,6-TNT)

TABLE 2-30.
METHOD 8331 - TETRAZENE

Tetrazene

TABLE 2-31
METHOD 8410 - SEMIVOLATILES

Acenaphthene
Acenaphthylene
Anthracene
Benzo(a)anthracene
Benzo(b)pyrene
Benzoic acid
Bis(2-chloroethoxy)methane
Bis(2-chloroethyl)ether
Bis(2-chloroisopropyl)ether
Bis(2-ethylhexyl)phthalate
4-Bromophenyl phenyl ether
Butyl benzyl phthalate
4-Chloroaniline
4-Chloro-3-methylphenol
2-Chloronaphthalene
2-Chlorophenol
4-Chlorophenol
4-Chlorophenyl phenyl ether
Chrysene
Dibenzofuran
Di-n-butyl phthalate
1,2-Dichlorobenzene
1,3-Dichlorobenzene
1,4-Dichlorobenzene
2,4-Dichlorophenol
Diethyl phthalate
Dimethyl phthalate
4,6-Dinitro-2-methylphenol
2,4-Dinitrophenol
2,4-Dinitrotoluene
2,6-Dinitrotoluene
Di-n-octyl phthalate
Di-n-propyl phthalate
Fluoranthene
Fluorene
Hexachlorobenzene
1,3-Hexachlorobutadiene
Hexachlorocyclopentadiene
Hexachloroethane
Isophorone
2-Methylnaphthalene
2-Methylphenol
4-Methylphenol
Naphthalene
2-Nitroaniline
3-Nitroaniline
4-Nitroaniline
Nitrobenzene
2-Nitrophenol
4-Nitrophenol
N-Nitrosodimethylamine
N-Nitrosodiphenylamine
N-Nitroso-di-n-propylamine
Pentachlorophenol
Phenanthrene
Phenol
Pyrene
1,2,4-Trichlorobenzene
2,4,5-Trichlorophenol
2,4,6-Trichlorophenol

TABLE 2-32.
ANALYSIS METHODS FOR INORGANIC COMPOUNDS

Compound	Applicable Method(s)
Aluminum	6010, 6020, 7020
Antimony	6010, 6020, 7040, 7041, 7062
Arsenic	6010, 6020, 7060, 7061, 7062
Barium	6010, 6020, 7080, 7081
Beryllium	6010, 6020, 7090, 7091
Bromide	9056
Cadmium	6010, 6020, 7130,7131
Calcium	6010, 7140
Chloride	9056, 9250, 9251, 9252, 9253
Chromium	6010, 6020, 7190, 7191
Chromium, hexavalent	7195, 7196, 7197, 7198
Cobalt	6010, 6020, 7200, 7201
Copper	6010, 6020, 7210, 7211
Cyanide	9010, 9012, 9013
Fluoride	9056
Iron	6010, 7380, 7381
Lead	6010, 6020, 7420, 7421
Lithium	6010, 7430
Magnesium	6010, 7450
Manganese	6010, 6020, 7460, 7461
Mercury	7470, 7471
Molybdenum	6010, 7480, 7481
Nickel	6010, 6020, 7520
Nitrate	9056, 9200
Nitrite	9056
Osmium	7550
Phosphate	9056
Phosphorus	6010
Potassium	6010, 7610
Selenium	6010, 7740, 7741, 7742
Silver	6010, 6020, 7760, 7761
Sodium	6010, 7770
Strontium	6010, 7780
Sulfate	9035, 9036, 9038, 9056
Sulfide	9030, 9031
Thallium	6010, 6020, 7840, 7841
Tin	7870
Vanadium	6010, 7910, 7911
Zinc	6010, 6020, 7950, 7951

TABLE 2-33.
CONTAINERS, PRESERVATION TECHNIQUES, AND HOLDING TIMES FOR AQUEOUS MATRICES[A]

Name	Container[1]	Preservation	Maximum holding time
Bacterial Tests:			
Coliform, total	P, G	Cool, 4°C, 0.008% $Na_2S_2O_3$	6 hours
Inorganic Tests:			
Chloride	P, G	None required	28 days
Cyanide, total and amenable to chlorination	P, G	Cool, 4°C; if oxidizing agents present add 5 mL 0.1N $NaAsO_2$ per L or 0.06 g of ascorbic acid per L; adjust pH>12 with 50% NaOH. See Method 9010 for other interferences.	14 days
Hydrogen ion (pH)	P, G	None required	24 hours
Nitrate	P, G	Cool, 4°C	48 hours
Sulfate	P, G	Cool, 4°C	28 days
Sulfide	P, G	Cool, 4°C, add zinc acetate	7 days
Metals:			
Chromium VI	P, G	Cool, 4°C	24 hours
Mercury	P, G	HNO_3 to pH<2	28 days
Metals, except chromium VI and mercury	P, G	HNO_3 to pH<2	6 months
Organic Tests:			
Acrolein and acrylonitrile	G, Teflon-lined septum	Cool, 4°C, 0.008% $Na_2S_2O_3$[3], Adjust pH to 4-5	14 days
Benzidines	G, Teflon-lined cap	Cool, 4°C, 0.008% Na_2S_2O3[3], Adjust pH to 6-9, store in dark	7 days until extraction, 40 days after extraction
Chlorinated hydrocarbons	G, Teflon-lined cap	Cool, 4°C, 0.008% $Na_2S_2O_3$[3]	7 days until extraction, 40 days after extraction
Dioxins and Furans	G, Teflon-lined cap	Cool, 4°C, 0.008% $Na_2S_2O_3$[3]	7 days until extraction, 40 days after extraction
Haloethers	G, Teflon-lined cap	Cool, 4°C, 0.008% $Na_2S_2O_3$[3]	7 days until extraction, 40 days after extraction
Nitroaromatics and cyclic ketones	G, Teflon-lined cap	Cool, 4°C, 0.008% $Na_2S_2O_3$[3] store in dark	7 days until extraction, 40 days after extraction
Nitrosamines	G, Teflon-lined cap	Cool, 4°C, 0.008% $Na_2S_2O_3$[3], store in dark	7 days until extraction, 40 days after extraction
Oil and grease	G	Cool, 4°C[2]	28 days
Organic carbon, total (TOC)	P, G	Cool, 4°C[2]	28 days
PCBs	G, Teflon-lined cap	Cool, 4°C	7 days until extraction, 40 days after extraction
Pesticides	G, Teflon-lined cap	Cool, 4°C	7 days until extraction, 40 days after extraction
Phenols	G, Teflon-lined cap	Cool, 4°C, 0.008% Na_2S_2O3[3]	7 days until extraction, 40 days after extraction
Phthalate esters	G, Teflon-lined cap	Cool, 4°C	7 days until extraction, 40 days after extraction
Polynuclear aromatic hydrocarbons	G, Teflon-lined cap	Cool, 4°C, 0.008% $Na_2S_2O_3$[3] store in dark	7 days until extraction, 40 days after extraction
Purgeable aromatic hydrocarbons	G, Teflon-lined septum	Cool, 4°C, 0.008% $Na_2S_2O_3$[2,3]	14 days
Purgeable Halocarbons	G, Teflon-lined septum	Cool, 4°C, 0.008% $Na_2S_2O_3$[3]	14 days
Total organic halides (TOX)	G, Teflon-lined cap	Cool, 4°C[2]	28 days
Radiological Tests:			
Alpha, beta and radium	P, G	HNO_3 to pH<2	6 months

[A] Table excerpted, in part, from Table II, 49 FR 209, October 26, 1984, p 28.
[1] Polyethylene (P) or Glass (G)
[2] Adjust to pH<2 with H_2SO_4, HCl or solid $NaHSO_4$.
[3] Free chlorine must be removed prior to addition of HCl by the appropriate addition of $Na_2S_2O_3$.

TABLE 2-34. PREPARATION METHODS FOR ORGANIC ANALYTES

	Aqueous (pH)[3]	Solids	Sludges Emulsions[1] (pH)[3]	Oils
Acids	3510 3520 (pH ≤2)	3540, 3541 3550 3580[2]	3520 (pH ≤2)	3650 3580[2]
Acrolein Acrylonitrile Acetonitrile	5030	5030	5030	5030
Aromatic Volatiles	5030	5030	5030	5030
Base/Neutral	3510 3520 (pH >11)	3540 3541 3550 3580[2]	3520 (pH >11)	3650 3580[2]
Chlorinated Herbicides	8150 8151 (pH ≤2)	8150 8151 3580[2]	8150 8151 (pH ≤2)	3580[2]
Chlorinated Hydrocarbons	3510 3520 (pH 7)	3540 3541 3550 3580[2]	3520 (pH 7)	3580[2]
Halogenated Volatiles	5030	5030	5030	5030
Nitroaromatic and Cyclic Ketones	3510 3520 (pH 5-9)	3540 3541 3550 3580[2]	3520 (pH 5-9)	3580[2]
Non-halogenated Volatiles	5030	5030	5030	5030
Organochlorine Pesticides and PCBs	3510 3520 3665 (pH 5-9)	3540 3541 3580[2] 3665	3520 (pH 5-9)	3580[2]
Organophosphorus Pesticides	3510 3520 (pH 6-8)	3540 3541 3580[2]	3520 (pH 6-8)	3580[2]
Phenols	3510 3520 (pH ≤2)	3540 3541 3550 3580[2]	3520 (pH ≤2)	3650 3580[2]
Phthalate Esters	3510 3520 (pH 7)	3540 3541 3550 3580[2]	3520 (pH 7)	3580[2]
Polynuclear Aromatic Hydrocarbons	3510 3520 (pH 7)	3540, 3541 3550 3580[2]	3520 (pH 7)	3560 3580[2]
Volatile Organics	5030	5030	5030	5030

[1] If attempts to break up emulsions are unsuccessful, these methods may be used.
[2] Method 3580 is only appropriate if the sample is soluble in the specified solvent.
[3] pH at which extraction should be performed.

TABLE 2-35.
CLEANUP OF ORGANIC ANALYTE EXTRACTS

Analyte Type	Method(s)
Acids	3650
Base/Neutral	3650
Chlorinated Herbicides	8150 8151
Chlorinated Hydrocarbons	3620 3640
Nitroaromatics & Cyclic Ketones	3620 3640
Organophosphorus Pesticides	3620
Organochlorine Pesticides & PCBs	3620 3630 3640 3660 3665
Phenols	3630 3640 3650
Phthalate Esters	3610 3611 3620 3640
Polynuclear Aromatic Hydrocarbons	3610 3611 3630 3640

TABLE 2-36.
DETERMINATION OF ORGANIC ANALYTES

	GC/MS Determination Methods	Specific GC Detection Methods	HPLC
SEMIVOLATILES			
Acids	8270 8250		
Base/Neutral	8270 8250		
Carbamates			8318
Chlorinated Herbicides	8270*	8150 8151	
Chlorinated Hydrocarbons	8270 8250	8120 8121	
Dyes			8321
Explosives			8330 8331
Haloethers	8270 8250	8110	
Nitroaromatics and Cyclic Ketones	8270 8250	8090	
Nitrosoamines	8270 8250	8070	
Organochlorine Pesticides and PCBs	8270*	8080 8081	
Organophosphorous Pesticides	8270*	8140 8141	8321
Phenols	8270 8250	8040	
Phthalate Esters	8270 8250	8060 8061	
Polynuclear Aromatic Hydrocarbons	8270 8250	8100	8310
VOLATILES			
Acrolein, Acrylonitrile, Acetonitrile	8240 8260	8030 8031	8316 8315
Acrylamide		8032	8316
Aromatic Volatiles	8240 8260	8020 8021	
Formaldehyde			8315
Halogenated Volatiles	8240 8260	8010 8011 8021	
Non-halogenated Volatiles	8240	8015	
Volatile Organics	8240 8260	8010 8011 8020 8021 8030 8031	8315 8316

*This method is an alternative confirmation method. It is not the method of choice.

FIGURE 2-1.
ORGANIC ANALYSIS OPTIONS

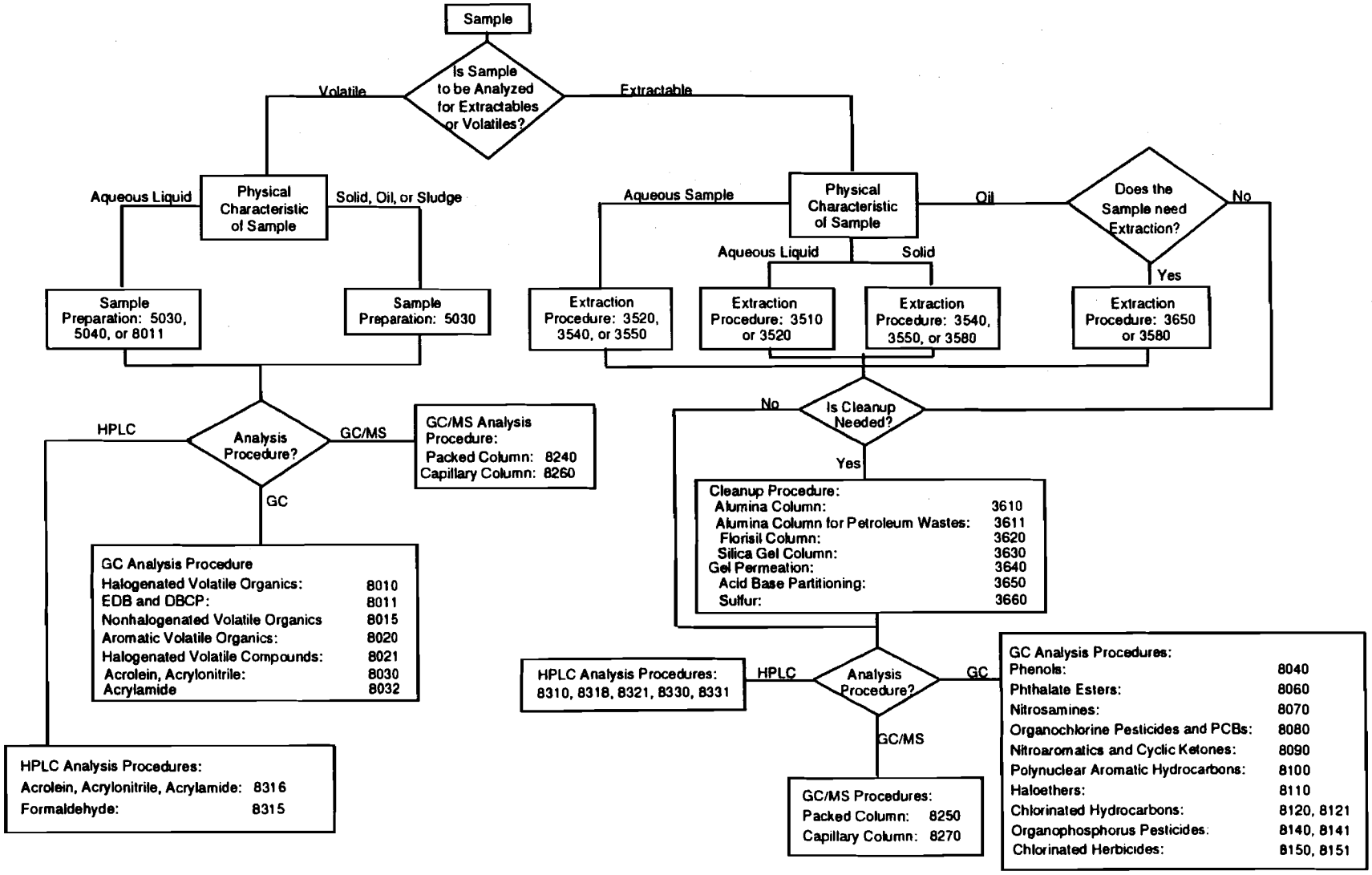


FIGURE 2-2.
SCHEMATIC OF SEQUENCE TO DETERMINE
IF A WASTE IS HAZARDOUS BY CHARACTERISTIC

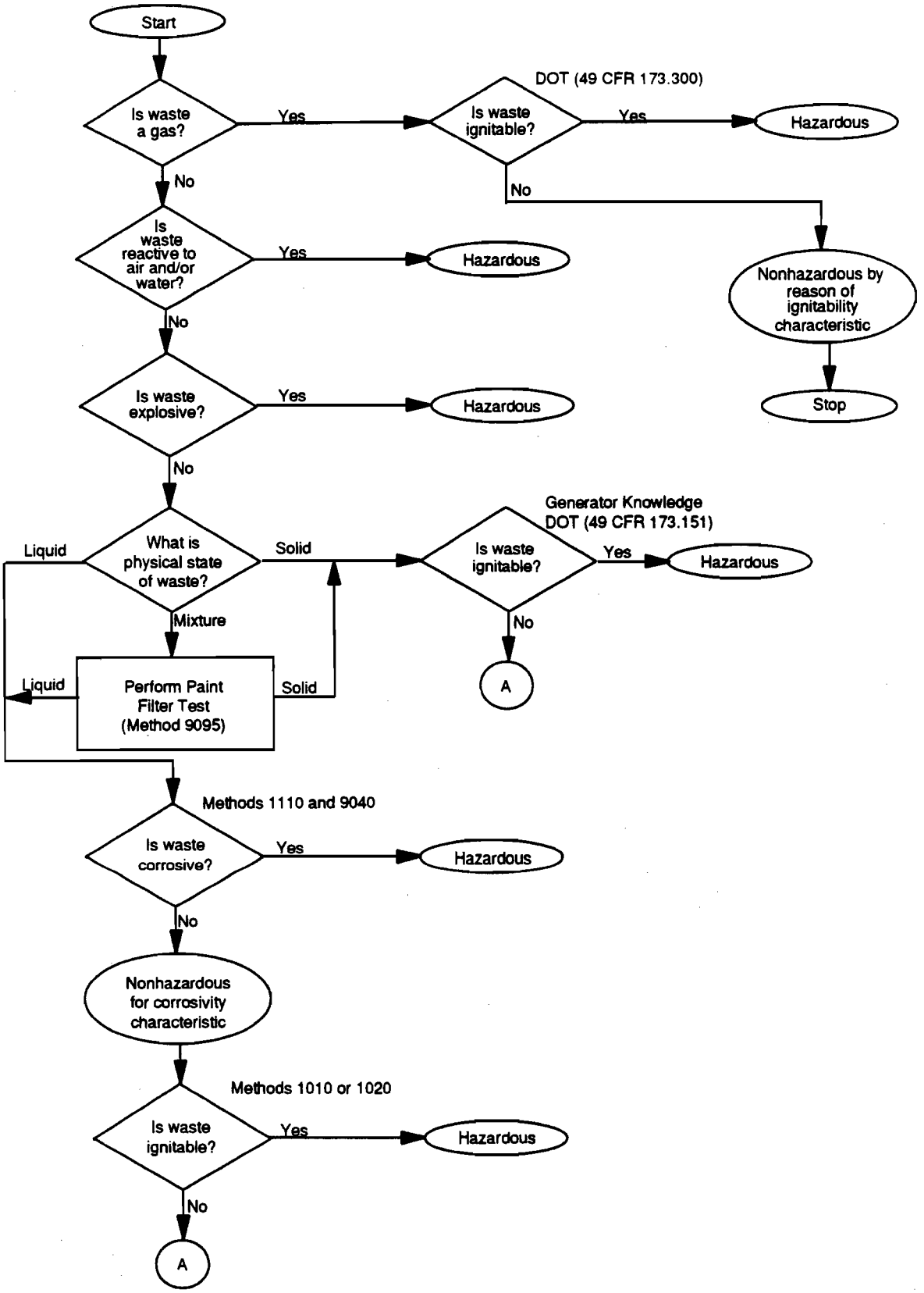


FIGURE 2-2.
(Continued)

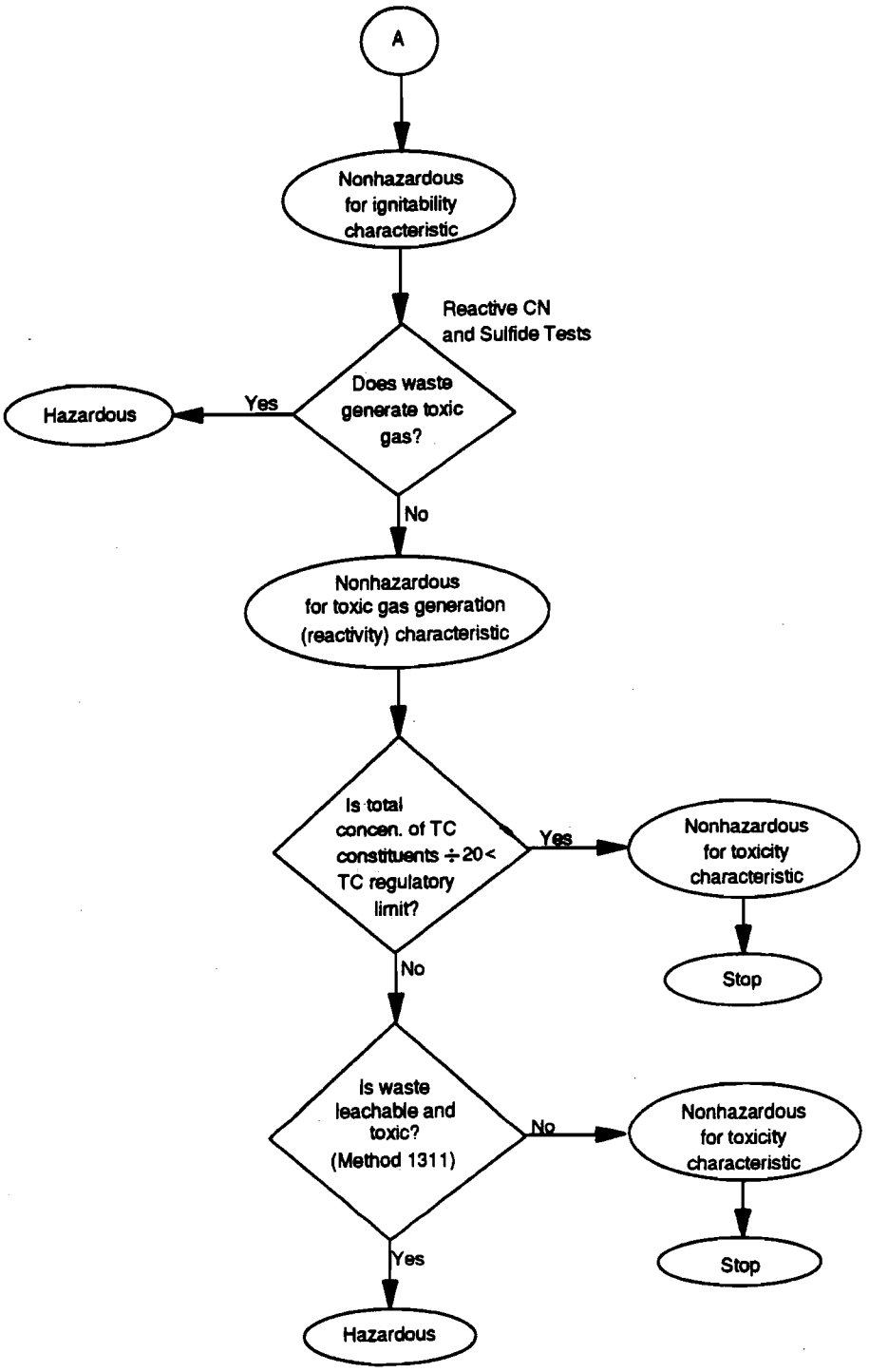


FIGURE 2-3A.
EP

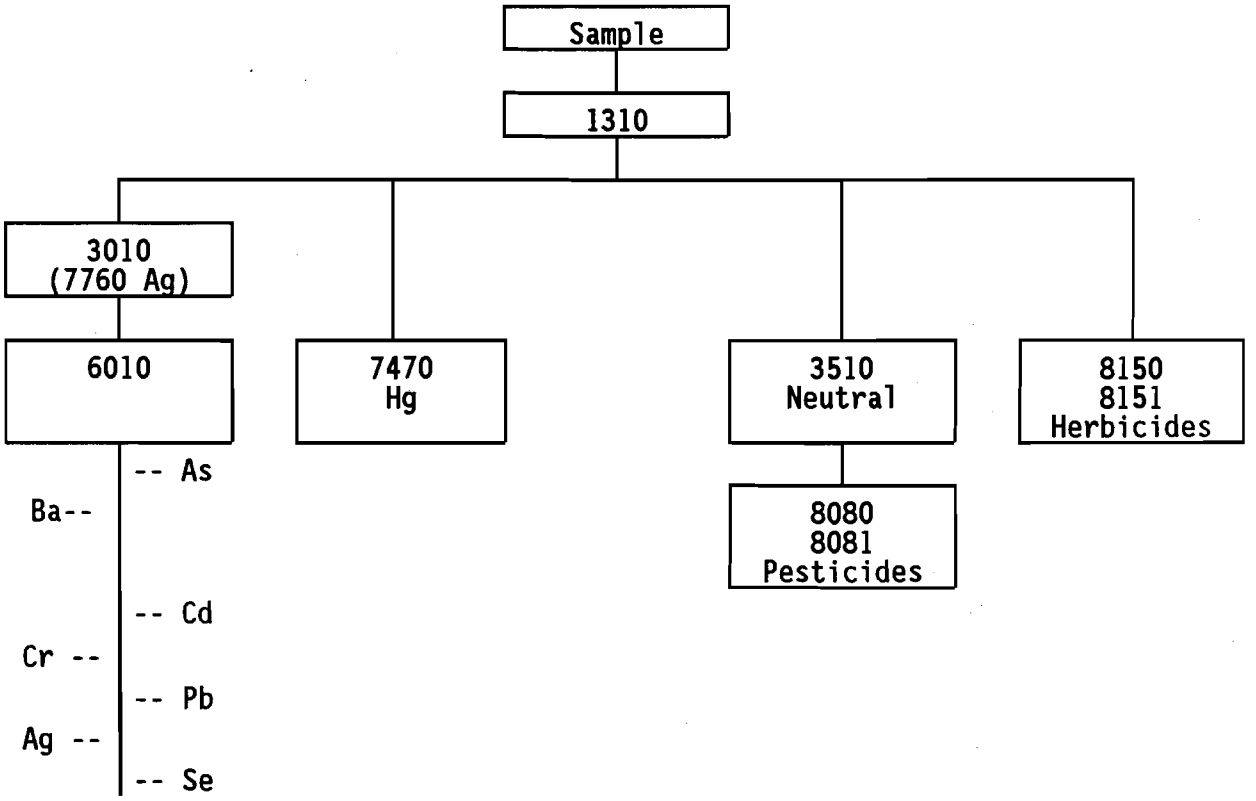


FIGURE 2-3B.
RECOMMENDED SW-846 METHODS OF ANALYSIS FOR TCLP LEACHATES

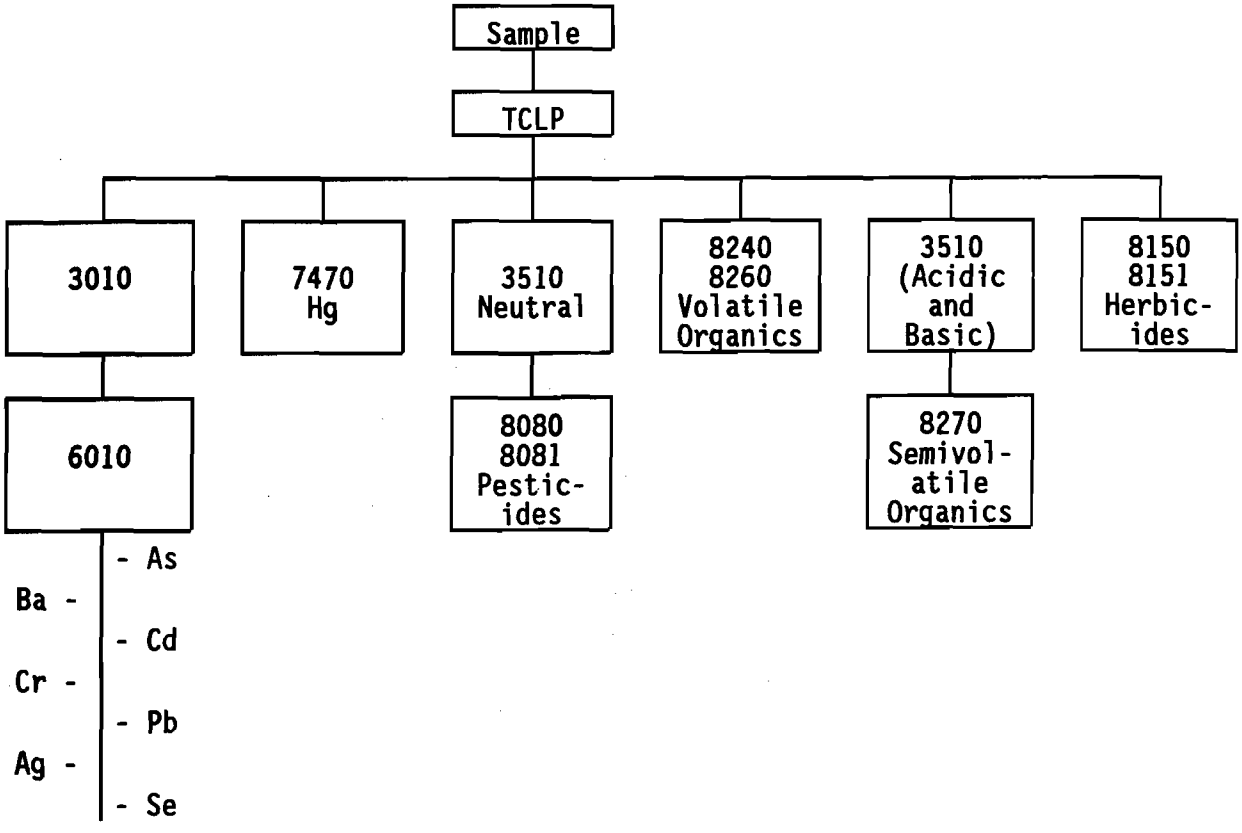
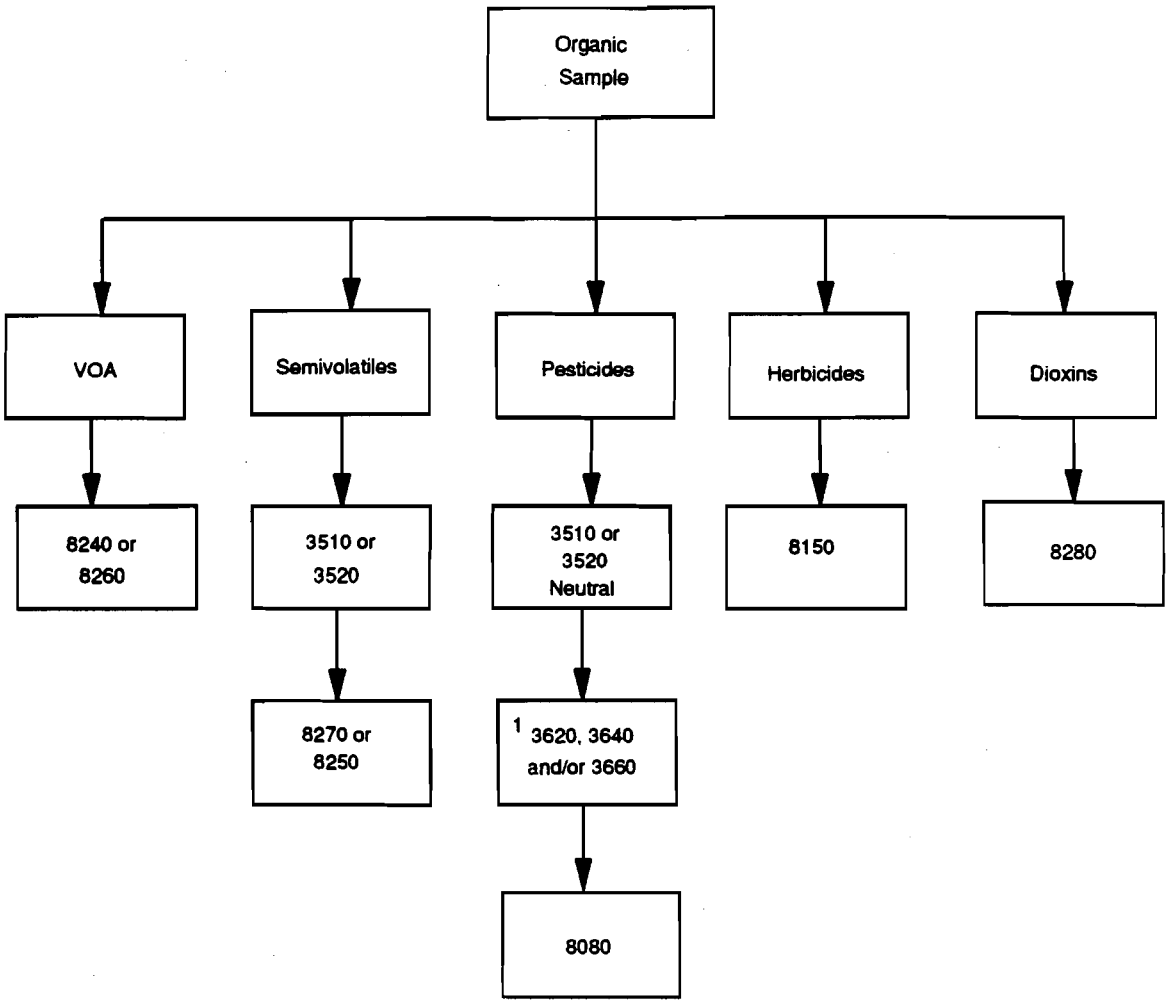
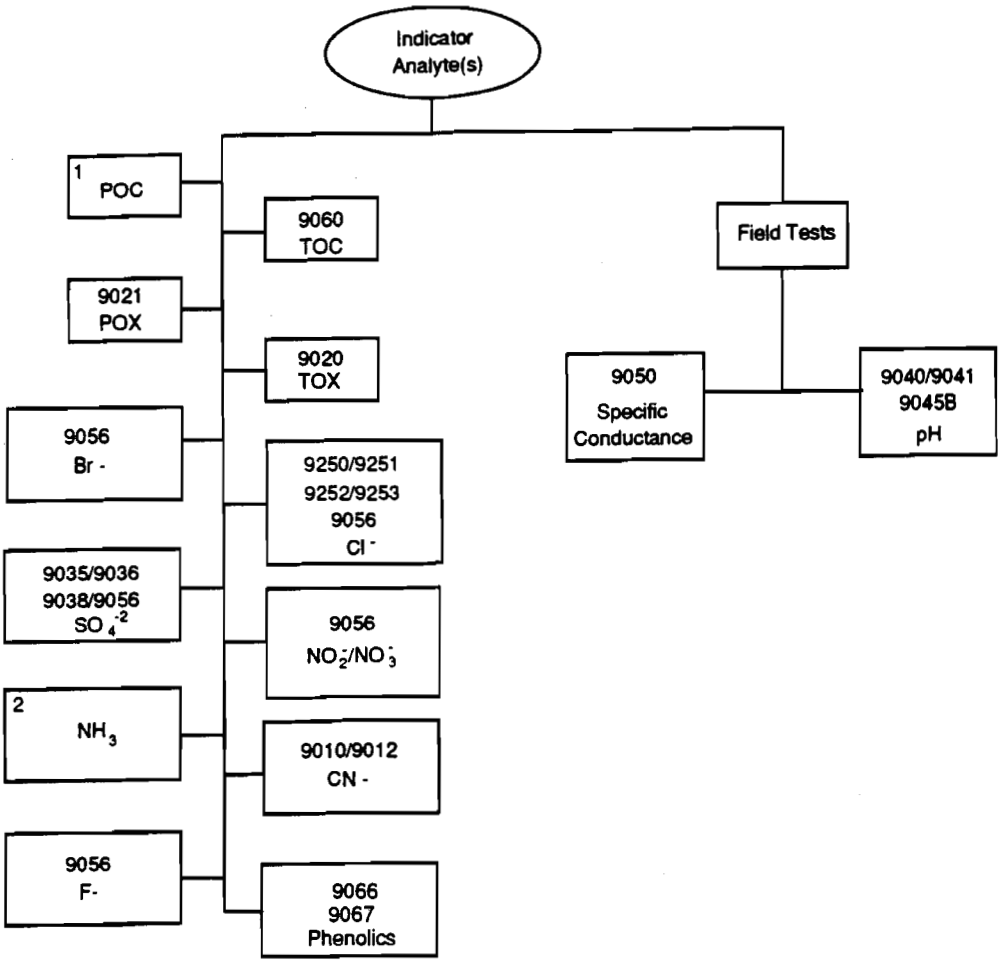


FIGURE 2-4A.
GROUND WATER ANALYSIS



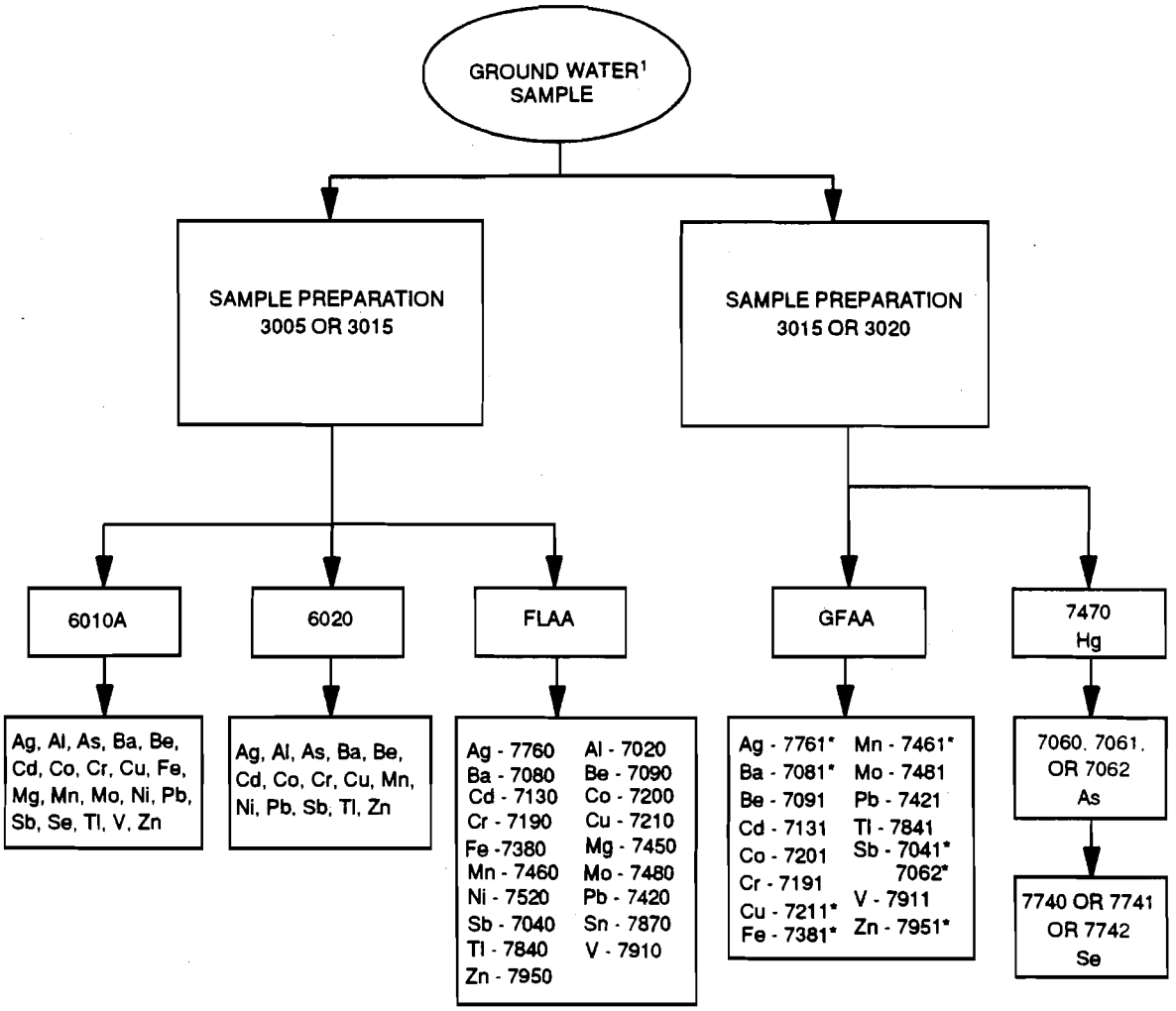
1 - Optional: Cleanup required only if interferences prevent analysis

FIGURE 2-4B.
INDICATOR ANALYTE



1 - Barcelona, 1984, (See Reference 1)
2 - Riggin, 1984, (See Reference 2)

FIGURE 2-4C.
GROUND WATER



* Follow the digestion procedures as detailed in the individual determinative methods.

[1] When analyzing for total dissolved metals, digestion is not necessary if the samples are filtered at the time of collection, and then acidified to the same concentration as the standards.

CHAPTER THREE

METALLIC ANALYTES

3.1 SAMPLING CONSIDERATIONS

3.1.1 Introduction

This manual contains procedures for the analysis of metals in a variety of matrices. These methods are written as specific steps in the overall analysis scheme -- sample handling and preservation, sample digestion or preparation, and sample analysis for specific metal components. From these methods, the analyst must assemble a total analytical protocol which is appropriate for the sample to be analyzed and for the information required. This introduction discusses the options available in general terms, provides background information on the analytical techniques, and highlights some of the considerations to be made when selecting a total analysis protocol.

3.1.2 Definition of Terms

Optimum concentration range: A range, defined by limits expressed in concentration, below which scale expansion must be used and above which curve correction should be considered. This range will vary with the sensitivity of the instrument and the operating conditions employed.

Sensitivity: a) Atomic Absorption: The concentration in milligrams of metal per liter that produces an absorption of 1%; b) Inductively Coupled Plasma (ICP): The slope of the analytical curve, i.e., the functional relationship between emission intensity and concentration.

Method detection limit (MDL): The minimum concentration of a substance that can be measured and reported with 99% confidence that the analyte concentration is greater than zero. The MDL is determined from analysis of a sample in a given matrix containing analyte which has been processed through the preparative procedure.

Total recoverable metals: The concentration of metals in an unfiltered sample following treatment with hot dilute mineral acid (Method 3005).

Dissolved metals: The concentration of metals determined in a sample after the sample is filtered through a 0.45-um filter (Method 3005).

Suspended metals: The concentration of metals determined in the portion of a sample that is retained by a 0.45-um filter (Method 3005).

Total metals: The concentration of metals determined in a sample following digestion by Methods 3010, 3015, 3020, 3050 or 3051.

Instrument detection limit (IDL): The concentration equivalent to a signal due to the analyte which is equal to three times the standard deviation of a series of 7 replicate measurements of a reagent blank's signal at the same wavelength.

Interference check sample (ICS): A solution containing both interfering and analyte elements of known concentration that can be used to verify background and interelement correction factors.

Initial calibration verification standard (ICV): A certified or independently prepared solution used to verify the accuracy of the initial calibration. For ICP analysis, it must be run at each wavelength used in the analysis.

Continuing calibration verification (CCV): Used to assure calibration accuracy during each analysis run. It must be run for each analyte as described in the particular analytical method. At a minimum, it should be analyzed at the beginning of the run and after the last analytical sample. Its concentration should be at or near the mid-range levels of the calibration curve.

Calibration standards: A series of known standard solutions used by the analyst for calibration of the instrument (i.e., preparation of the analytical curve).

Linear dynamic range: The concentration range over which the analytical curve remains linear.

Method blank: A volume of reagent water processed through each sample preparation procedure.

Calibration blank: A volume of reagent water acidified with the same amounts of acids as were the standards and samples.

Laboratory control standard: A volume of reagent water spiked with known concentrations of analytes and carried through the preparation and analysis procedure as a sample. It is used to monitor loss/recovery values.

Method of standard addition (MSA): The standard-addition technique involves the use of the unknown and the unknown plus several known amounts of standard. See Method 7000, Section 8.7 for detailed instructions.

Sample holding time: The storage time allowed between sample collection and sample analysis when the designated preservation and storage techniques are employed.

3.1.3 Sample Handling and Preservation

Sample holding times, digestion procedures and suggested collection volumes are listed in Table 1. The sample volumes required depend upon the number of different digestion procedures necessary for analysis. This may be determined by the application of graphite-furnace atomic absorption spectrometry (GFAA), flame atomic absorption spectrometry (FLAA), inductively coupled argon plasma emission spectrometry (ICP), hydride-generation atomic absorption spectrometry (HGAA), inductively coupled plasma mass spectrometry (ICP-MS) or cold-vapor atomic absorption spectrometry (CVAA) techniques, each of which may require different digestion procedures. The indicated volumes in Table 3-1 refer to that required for the individual digestion procedures and recommended sample collection volumes.

In the determination of trace metals, containers can introduce either positive or negative errors in the measurement of trace metals by (a) contributing contaminants through leaching or surface desorption, and (b) depleting concentrations through adsorption. Thus the collection and treatment of the sample prior to analysis require particular attention. The following cleaning treatment sequence has been determined to be adequate to minimize contamination in the sample bottle, whether borosilicate glass, linear polyethylene, polypropylene, or Teflon: detergent, tap water, 1:1 nitric acid, tap water, 1:1 hydrochloric acid, tap water, and reagent water.

> NOTE: **Chromic acid should not be used to clean glassware**, especially if chromium is to be included in the analytical scheme. Commercial, non-chromate products (e.g., Nochromix) may be used in place of chromic acid if adequate cleaning is documented by an analytical quality control program. (Chromic acid should also not be used with plastic bottles.)

3.1.4 Safety

The toxicity or carcinogenicity of each reagent used in these methods has not been precisely defined. However, each chemical compound should be treated as a potential health hazard. From this viewpoint, exposure to these chemicals must be reduced to the lowest possible level by whatever means available. The laboratory is responsible for maintaining a current awareness file of OSHA regulations regarding the safe handling of the chemicals specified in these methods. A reference file of material data-handling sheets should also be made available to all personnel involved in the chemical analysis. Additional references to laboratory safety are available. They are:

1. "Carcinogens - Working with Carcinogens," Department of Health, Education, and Welfare, Public Health Service, Center for Disease Control, National Institute for Occupational Safety and Health, Publication No. 77-206, August 1977.

TABLE 3-1.

SAMPLE HOLDING TIMES, REQUIRED DIGESTION VOLUMES AND RECOMMENDED COLLECTION VOLUMES FOR METAL DETERMINATIONS IN AQUEOUS AND SOLID SAMPLES

Measurement	Digestion Vol. Req.[a] (mL)	Collection Volume (mL)[a]	Treatment/ Preservative Holding Time[c]
Metals (except hexavalent chromium and mercury):			
Aqueous			
Total	100	600	HNO_3 to pH <2 6 months
Dissolved	100	600	Filter on site; HNO_3 to pH <2 6 months
Suspended	100	600	Filter on site 6 months
Solid			
Total	2g	200g	6 months
Chromium VI:[b]			
Aqueous	100	400	24 hr
Solid	---	200g	----
Mercury:			
Aqueous			
Total	100	400	HNO_3 to pH <2 28 days
Dissolved	100	400	Filter; HNO_3 to pH <2 28 days
Solid			
Total	0.2g	200g	28 days

[a]Unless stated otherwise.
[b]The holding time for the analysis of hexavalent chromium in solid samples has not yet been determined. A holding time of "as soon as possible" is recommended.
[c]All non-aqueous samples and all aqueous samples that are to be analyzed for mercury and hexavalent chromium must be stored at 4°C ± 2°C until analyzed, either glass or plastic containers may be used.

2. "OSHA Safety and Health Standards, General Industry" (29 CFR 1910), Occupational Safety and Health Administration, OSHA 2206, revised January 1976.

3. "Proposed OSHA Safety and Health Standards, Laboratories," Occupational Safety and Health Administration, Federal Register, July 24, 1986, p. 26660.

4. "Safety in Academic Chemistry Laboratories," American Chemical Society Publication, Committee on Chemical Safety, 3rd edition, 1979.

3.2 SAMPLE PREPARATION METHODS

The methods in SW-846 for sample digestion or preparation are as follows[1]:

Method 3005 prepares ground water and surface water samples for total recoverable and dissolved metals determination by FLAA, ICP-AES, or ICP-MS. The unfiltered or filtered sample is heated with dilute HCl and HNO_3 prior to metal determination.

Method 3010 prepares waste samples for total metal determination by FLAA, ICP-AES, or ICP-MS. The samples are vigorously digested with nitric acid followed by dilution with hydrochloric acid. The method is applicable to aqueous samples, EP and mobility-procedure extracts.

Method 3015 prepares aqueous samples, mobility-procedure extracts, and wastes that contain suspended solids for total metal determination by FLAA, GFAA, ICP-AES, or ICP-MS. Nitric acid is added to the sample in a Teflon digestion vessel and heated in a microwave unit prior to metals determination.

Method 3020 prepares waste samples for total metals determination by furnace GFAA or ICP-MS. The samples are vigorously digested with nitric acid followed by dilution with nitric acid. The method is applicable to aqueous samples, EP and mobility-procedure extracts.

Method 3040 prepares oily waste samples for determination of soluble metals by FLAA, GFAA, and ICP-AES methods. The samples are dissolved and diluted in organic solvent prior to analysis. The method is applicable to the organic extract in the oily waste EP procedure and other samples high in oil, grease, or wax content.

Method 3050 prepares waste samples for total metals determination by FLAA and ICP-AES, or ICP-MS. The samples are vigorously digested in nitric acid and hydrogen peroxide followed by dilution with either nitric or hydrochloric acid. The method is applicable to soils, sludges, and solid waste samples.

Method 3051 prepares sludges, sediments, soils and oils for total metals determination by FLAA, GFAA, ICP-AES or ICP-MS. Nitric acid is added to

the representative sample in a Teflon digestion vessel and heated in a microwave unit prior to metals determination.

[1] Please note that chlorine is an interferent in ICP-MS analyses and its use should be discouraged except when absolutely necessary.

METHOD 3005A

ACID DIGESTION OF WATERS FOR TOTAL RECOVERABLE OR DISSOLVED METALS FOR ANALYSIS BY FLAA OR ICP SPECTROSCOPY

1.0 SCOPE AND APPLICATION

1.1 Method 3005 is an acid digestion procedure used to prepare surface and ground water samples for analysis by flame atomic absorption spectroscopy (FLAA) or by inductively coupled argon plasma spectroscopy (ICP). Samples prepared by Method 3005 may be analyzed by AAS or ICP for the following metals:

Aluminum	Magnesium
Antimony**	Manganese
Arsenic*	Molybdenum
Barium	Nickel
Beryllium	Potassium
Cadmium	Selenium*
Calcium	Silver
Chromium	Sodium
Cobalt	Thallium
Copper	Vanadium
Iron	Zinc
Lead	

* ICP only
**May be analyzed by ICP, FLAA, or GFAA

1.2 When analyzing for total dissolved metals filter the sample, at the time of collection, prior to acidification with nitric acid.

2.0 SUMMARY OF METHOD

2.1 Total recoverable metals - The entire sample is acidified at the time of collection with nitric acid. At the time of analysis the sample is heated with acid and substantially reduced in volume. The digestate is filtered and diluted to volume, and is then ready for analysis.

2.2 Dissolved metals - The sample is filtered through a 0.45-μm filter at the time of collection and the liquid phase is then acidified at the time of collection with nitric acid. Samples for dissolved metals do not need to be digested as long as the acid concentrations have been adjusted to the same concentration as in the standards.

3.0 INTERFERENCES

3.1 The analyst should be cautioned that this digestion procedure may not be sufficiently vigorous to destroy some metal complexes.

Precipitation will cause a lowering of the silver concentration and therefore an inaccurate analysis.

4.0 APPARATUS AND MATERIALS

4.1 Griffin beakers of assorted sizes or equivalent.

4.2 Watch glasses or equivalent.

4.3 Qualitative filter paper and filter funnels.

4.4 Graduated cylinder or equivalent.

4.5 Electric hot plate or equivalent - adjustable and capable of maintaining a temperature of 90-95°C.

5.0 REAGENTS

5.1 Reagent grade chemicals shall be used in all tests. Unless otherwise indicated, it is intended that all reagents shall conform to the specifications of the Committee on Analytical Reagents of the American Chemical Society, where such specifications are available. Other grades may be used, provided it is first ascertained that the reagent is of sufficiently high purity to permit its use without lessening the accuracy of the determination.

5.2 Reagent Water. Reagent water shall be interference free. All references to water in the method refer to reagent water unless otherwise specified. Refer to Chapter One for a definition of reagent water.

5.3 Nitric acid (concentrated), HNO_3. Acid should be analyzed to determine level of impurities. If method blank is < MDL, then acid can be used.

5.4 Hydrochloric acid (concentrated), HCl. Acid should be analyzed to determine level of impurities. If method blank is < MDL, then acid can be used.

6.0 SAMPLE COLLECTION, PRESERVATION, AND HANDLING

6.1 All samples must have been collected using a sampling plan that addresses the considerations discussed in Chapter Nine of this manual.

6.2 All sample containers must be prewashed with detergents, acids, and water. Both plastic and glass containers are suitable.

6.3 Sampling

6.3.1 Total recoverable metals - All samples must be acidified at the time of collection with HNO_3 (5 mL/L).

6.3.2 Dissolved metals - All samples must be filtered through a 0.45-μm filter and then acidified at the time of collection with HNO_3 (5 mL/L).

7.0 PROCEDURE

7.1 Transfer a 100-mL aliquot of well-mixed sample to a beaker.

7.2 For metals that are to be analyzed, add 2 mL of concentrated HNO_3 and 5 mL of concentrated HCl. The sample is covered with a ribbed watch glass or other suitable covers and heated on a steam bath, hot plate or other heating source at 90 to 95°C until the volume has been reduced to 15-20 mL.

CAUTION: Do not boil. Antimony is easily lost by volatilization from hydrochloric acid media.

7.3 Remove the beaker and allow to cool. Wash down the beaker walls and watch glass with water and, when necessary, filter or centrifuge the sample to remove silicates and other insoluble material that could clog the nebulizer. Filtration should be done only if there is concern that insoluble materials may clog the nebulizer; this additional step is liable to cause sample contamination unless the filter and filtering apparatus are thoroughly cleaned and prerinsed with dilute HNO_3.

7.4 Adjust the final volume to 100 mL with reagent water.

8.0 QUALITY CONTROL

8.1 All quality control measures described in Chapter One should be followed.

8.2 For each analytical batch of samples processed, blanks should be carried throughout the entire sample preparation and analytical process. These blanks will be useful in determining if samples are being contaminated. Refer to Chapter One for the proper protocol when analyzing blanks.

8.3 Replicate samples should be processed on a routine basis. A replicate sample is a sample brought through the whole sample preparation and analytical process. Replicate samples will be used to determine precision. The sample load will dictate the frequency, but 5% is recommended. Refer to Chapter One for the proper protocol when analyzing replicates.

8.4 Spiked samples or standard reference materials should be employed to determine accuracy. A spiked sample should be included with each batch. Refer to Chapter One for the proper protocol when analyzing spikes.

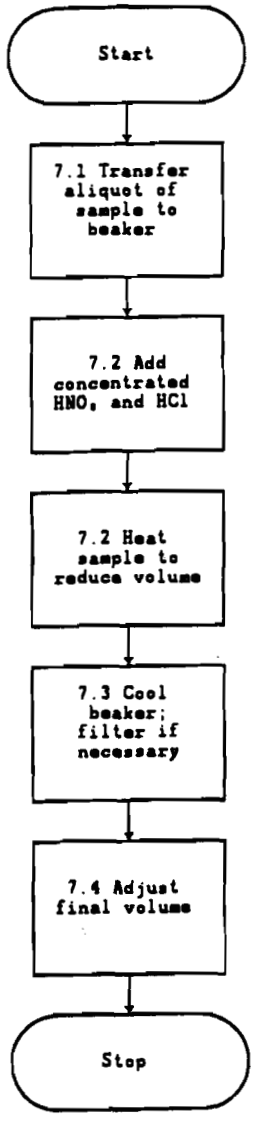
9.0 METHOD PERFORMANCE

9.1 No data provided.

10.0 REFERENCES

1. Rohrbough, W.G.; et al. Reagent Chemicals, American Chemical Society Specifications, 7th ed.; American Chemical Society: Washington, DC, 1986.

2. 1985 Annual Book of ASTM Standards, Vol. 11.01; "Standard Specification for Reagent Water"; ASTM: Philadelphia, PA, 1985; D1193-77.


Start
7.1 Transfer aliquot of sample to beaker
7.2 Add concentrated HNO_3 and HCl
7.2 Heat sample to reduce volume
7.3 Cool beaker; filter if necessary
7.4 Adjust final volume
Stop

METHOD 3010A

ACID DIGESTION OF AQUEOUS SAMPLES AND EXTRACTS FOR TOTAL METALS FOR ANALYSIS BY FLAA OR ICP SPECTROSCOPY

1.0 SCOPE AND APPLICATION

1.1 This digestion procedure is used for the preparation of aqueous samples, EP and mobility-procedure extracts, and wastes that contain suspended solids for analysis, by flame atomic absorption spectroscopy (FLAA) or inductively coupled argon plasma spectroscopy (ICP). The procedure is used to determine total metals.

1.2 Samples prepared by Method 3010 may be analyzed by FLAA or ICP for the following:

Aluminum	Magnesium
*Arsenic	Manganese
Barium	Molybdenum
Beryllium	Nickel
Cadmium	Potassium
Calcium	*Selenium
Chromium	Sodium
Cobalt	Thallium
Copper	Vanadium
Iron	Zinc
Lead	

* Analysis by ICP

NOTE: See Method 7760 for the digestion and FLAA analysis of Silver.

1.3 This digestion procedure is not suitable for samples which will be analyzed by graphite furnace atomic absorption spectroscopy because hydrochloric acid can cause interferences during furnace atomization. Consult Method 3020A for samples requiring graphite furnace analysis.

2.0 SUMMARY OF METHOD

2.1 A mixture of nitric acid and the material to be analyzed is refluxed in a covered Griffin beaker. This step is repeated with additional portions of nitric acid until the digestate is light in color or until its color has stabilized. After the digestate has been brought to a low volume, it is refluxed with hydrochloric acid and brought up to volume. If sample should go to dryness, it must be discarded and the sample reprepared.

3.0 INTERFERENCES

3.1 Interferences are discussed in the referring analytical method.

4.0 APPARATUS AND MATERIALS

4.1 Griffin beakers - 150-mL or equivalent.

4.2 Watch glasses - Ribbed and plain or equivalent.

4.3 Qualitative filter paper or centrifugation equipment.

4.4 Graduated cylinder or equivalent - 100mL.

4.5 Funnel or equivalent.

4.6 Hot plate or equivalent heating source - adjustable and capable of maintaining a temperature of 90-95°C.

5.0 REAGENTS

5.1 Reagent grade chemicals shall be used in all tests. Unless otherwise indicated, it is intended that all reagents shall conform to the specifications of the Committee on Analytical Reagents of the American Chemical Society, where such specifications are available. Other grades may be used, provided it is first ascertained that the reagent is of sufficiently high purity to permit its use without lessening the accuracy of the determination.

5.2 Reagent Water. Reagent water will be interference free. All references to water in the method refer to reagent water unless otherwise specified. Refer to Chapter One for a definition of reagent water.

5.3 Nitric acid (concentrated), HNO_3. Acid should be analyzed to determine levels of impurities. If method blank is < MDL, the acid can be used.

5.4 Hydrochloric acid (1:1), HCl. Prepared from water and hydrochloric acid. Hydrochloric acid should be analyzed to determine level of impurities. If method blank is < MDL, the acid can be used.

6.0 SAMPLE COLLECTION, PRESERVATION, AND HANDLING

6.1 All samples must have been collected using a sampling plan that addresses the considerations discussed in Chapter Nine of this manual.

6.2 All sample containers must be prewashed with detergents, acids, and water. Plastic and glass containers are both suitable. See Chapter Three, Step 3.1.3, for further information.

6.3 Aqueous wastewaters must be acidified to a pH of < 2 with HNO_3.

7.0 PROCEDURE

7.1 Transfer a 100-mL representative aliquot of the well-mixed sample to a 150-mL Griffin beaker and add 3 mL of concentrated HNO_3. Cover the beaker with a ribbed watch glass or equivalent. Place the beaker on a hot plate or

equivalent heating source and cautiously evaporate to a low volume (5 mL), making certain that the sample does not boil and that no portion of the bottom of the beaker is allowed to go dry. Cool the beaker and add another 3-mL portion of concentrated HNO_3. Cover the beaker with a nonribbed watch glass and return to the hot plate. Increase the temperature of the hot plate so that a gentle reflux action occurs.

NOTE: If a sample is allowed to go to dryness, low recoveries will result. Should this occur, discard the sample and reprepare.

7.2 Continue heating, adding additional acid as necessary, until the digestion is complete (generally indicated when the digestate is light in color or does not change in appearance with continued refluxing). Again, uncover the beaker or use a ribbed watch glass, and evaporate to a low volume (3 mL), not allowing any portion of the bottom of the beaker to go dry. Cool the beaker. Add a small quantity of 1:1 HCl (10 mL/100 mL of final solution), cover the beaker, and reflux for an additional 15 minutes to dissolve any precipitate or residue resulting from evaporation.

7.3 Wash down the beaker walls and watch glass with water and, when necessary, filter or centrifuge the sample to remove silicates and other insoluble material that could clog the nebulizer. Filtration should be done only if there is concern that insoluble materials may clog the nebulizer. This additional step can cause sample contamination unless the filter and filtering apparatus are thoroughly cleaned. Rinse the filter and filter apparatus with dilute nitric acid and discard the rinsate. Filter the sample and adjust the final volume to 100 mL with reagent water and the final acid concentration to 10%. The sample is now ready for analysis.

8.0 QUALITY CONTROL

8.1 All quality control measures described in Chapter One should be followed.

8.2 For each analytical batch of samples processed, blanks should be carried throughout the entire sample-preparation and analytical process. These blanks will be useful in determining if samples are being contaminated. Refer to Chapter One for the proper protocol when analyzing blanks.

8.3 Replicate samples should be processed on a routine basis. A replicate sample is a sample brought through the whole sample preparation and analytical process. A replicate sample should be processed with each analytical batch or every 20 samples, whichever is greater. Refer to Chapter One for the proper protocol when analyzing replicates.

8.4 Spiked samples or standard reference materials should be employed to determine accuracy. A spiked sample should be included with each batch of samples processed and whenever a new sample matrix is being analyzed. Refer to Chapter One for the proper protocol when analyzing spikes.

8.5 The method of standard addition shall be used for the analysis of all EP extracts and delisting petitions (see Method 7000, Step 8.7). Although not required, use of the method of standard addition is recommended for any sample

that is suspected of having an interference.

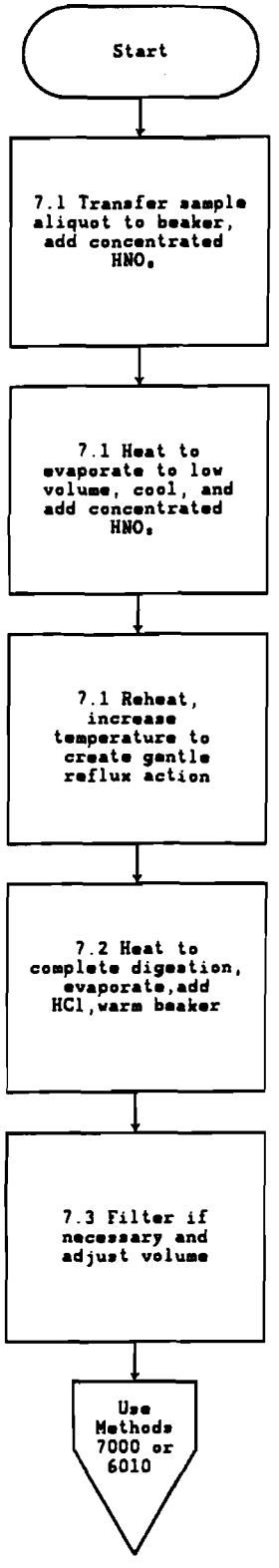
9.0 METHOD PERFORMANCE

9.1 No data provided.

10.0 REFERENCES

1. Rohrbough, W.G.; et al. Reagent Chemicals, American Chemical Society Specifications, 7th ed.; American Chemical Society: Washington, DC, 1986.

2. 1985 Annual Book of ASTM Standards, Vol. 11.01; "Standard Specification for Reagent Water"; ASTM: Philadelphia, PA, 1985; D1193-77.


Start
7.1 Transfer sample aliquot to beaker, add concentrated HNO3
7.1 Heat to evaporate to low volume, cool, and add concentrated HNO3
7.1 Reheat, increase temperature to create gentle reflux action
7.2 Heat to complete digestion, evaporate,add HCl,warm beaker
7.3 Filter if necessary and adjust volume
Use Methods 7000 or 6010

METHOD 3015

MICROWAVE ASSISTED ACID DIGESTION OF AQUEOUS SAMPLES AND EXTRACTS

1.0 SCOPE AND APPLICATION

1.1 This digestion procedure is used for the preparation of aqueous samples, mobility-procedure extracts, and wastes that contain suspended solids for analysis, by flame atomic absorption spectroscopy (FLAA), graphite furnace absorption spectroscopy (GFAA), inductively coupled argon plasma spectroscopy (ICP), or inductively coupled argon plasma mass spectrometry (ICP-MS). The procedure is a hot acid leach for determining available metals. Due to the rapid advances in microwave technology, consult your manufacturer's recommended instructions for guidance on their microwave digestion system and refer to the SW-846 "DISCLAIMER" when conducting analyses using Method 3015.

1.2 Samples prepared by Method 3015 using nitric acid digestion may be analyzed by FLAA, GFAA, ICP-AES, or ICP-MS for the following:

Aluminum	Lead
Antimony	Magnesium
Arsenic*	Manganese
Barium	Molybdenum
Beryllium	Nickel
Cadmium	Potassium
Calcium	Selenium*
Chromium	Silver
Cobalt	Sodium
Copper	Thallium
Iron	Vanadium
	Zinc

*Cannot be analyzed by FLAA

2.0 SUMMARY OF METHOD

2.1 A representative 45 mL aqueous sample is digested in 5 mL of concentrated nitric acid in a fluorocarbon (PFA or TFM) digestion vessel for 20 minutes using microwave heating. After the digestion process, the sample is cooled, and then filtered, centrifuged, or allowed to settle in a clean sample bottle prior to analysis.

3.0 INTERFERENCES

3.1 Many samples that contain organics, such as TCLP extracts, will result in higher vessel pressures which have the potential to cause venting of the vessels. Venting can result in either loss of analytes and/or sample, which must be avoided. A smaller sample size can be used but the final water volume

prior to nitric acid addition must remain at 45 mL. This is required to retain the heat characteristics of the calibration procedure. Limits of quantitation will change with sample quantity (dilution) as with instrumentation."

4.0 APPARATUS AND MATERIALS

4.1 Microwave apparatus requirements

4.1.1 The microwave unit provides programmable power with a minimum of 574 W, which can be programmed to within ± 10 W of the required power. Typical units provide a nominal 600 W to 1200 W of power. Temperature monitoring and control of the microwave unit are desirable.

4.1.2 The microwave unit cavity is corrosion resistant and well ventilated.

4.1.3 All electronics are protected against corrosion for safe operation.

4.1.4 The system requires fluorocarbon (PFA or TFM) digestion vessels (120 mL capacity) capable of withstanding pressures up to 7.5 ± 0.7 atm (110 ± 10 psig) and capable of controlled pressure relief at pressures exceeding 7.5 ± 0.7 atm (110 ± 10 psig).

4.1.5 A rotating turntable is employed to insure homogeneous distribution of microwave radiation within the unit. The speed of the turntable should be a minimum of 3 rpm.

CAUTION: Those laboratories now using or contemplating the use of kitchen type microwave ovens for this method should be aware of several significant safety issues. First, when an acid such as nitric is used to assist sample digestion in microwave units in open vessels, or sealed vessels equipped with venting features, there is the potential for the acid gases released to corrode the safety devices that prevent the microwave magnetron from shutting off when the door is opened. This can result in operator exposure to microwave energy. Use of a unit with corrosion resistant safety devices prevents this from occurring.

CAUTION: The second safety concern relates to the use of sealed containers without pressure relief valves in the unit. Temperature is the important variable controlling the reaction. Pressure is needed to attain elevated temperatures but must be safely contained. However, many digestion vessels constructed from certain fluorocarbons may crack, burst, or explode in the oven under certain pressures. Only unlined fluorocarbon (PFA or TFM) containers with pressure relief mechanisms or containers with fluorocarbon (PFA or TFM) liners and pressure relief mechanisms are considered acceptable at present.

Users are therefore advised not to use kitchen type microwave ovens or to use sealed containers without pressure relief valves for microwave acid digestions by this method. Use of laboratory grade microwave equipment is required to prevent safety hazards. For further information consult reference 1.

CAUTION: In addition, there are many safety and operational recommendations specific to the model and manufacturer of the microwave equipment used in individual laboratories. These specific suggestions are beyond the scope of this method and require the analyst to consult the specific equipment manual, manufacturer and literature for proper and safe operation of the microwave equipment and vessels.

4.2 Volumetric graduated cylinder, 50 or 100 mL capacity or equivalent.

4.3 Filter paper, qualitative or equivalent.

4.4 Analytical balance, 300 g capacity, minimum accuracy ± 0.01 g.

4.5 Filter funnel, glass or disposable polypropylene.

5.0 REAGENTS

5.1 Reagent grade chemicals shall be used in all tests. Unless otherwise indicated, it is intended that all reagents shall conform to the specifications of the Committee on Analytical Reagents of the American Chemical Society, where such specifications are available. Other grades may be used, provided it is first ascertained that the reagent is of sufficiently high purity to permit its use without lessening the accuracy of the determination. If the purity of a reagent is questionable, analyze the reagent to determine the level of impurities. The reagent blank must be less than the MDL in order to be used.

5.2 Reagent Water. Reagent water shall be interference free. All references to water in the method refer to reagent water unless otherwise specified (Ref. 2).

5.3 Concentrated nitric acid, HNO_3. Acid should be analyzed to determine levels of impurities. If the method blank is less than the MDL, the acid can be used.

6.0 SAMPLE COLLECTION, PRESERVATION, AND HANDLING

6.1 All samples must have been collected using a sampling plan that addresses the considerations discussed in Chapter Nine of this manual.

6.2 All sample containers must be prewashed with detergents, acids, and water. Plastic containers are preferable. See Chapter Three, Step 3.1.3 of this manual, for further information.

6.3 Aqueous waste waters must be acidified to a pH of < 2 with HNO_3.

7.0 PROCEDURE

7.1 Calibration of Microwave Equipment

NOTE: If the microwave unit uses temperature feedback control capable of replicating the performance specifications of the method, then the calibration procedure may be omitted.

7.1.1 Measurement of the available power for heating is evaluated so that absolute power in watts may be transferred from one microwave unit to another. For cavity type microwave equipment, this is accomplished by measuring the temperature rise in 1 kg of water exposed to microwave radiation for a fixed period of time. The analyst can relate power in watts to the partial power setting of the unit. The calibration format required for laboratory microwave units depends on the type of electronic system used by the manufacturer to provide partial microwave power. Few units have an accurate and precise linear relationship between percent power settings and absorbed power. Where linear circuits have been utilized, the calibration curve can be determined by a three-point calibration method (7.1.3), otherwise, the analyst must use the multiple point calibration method (7.1.2).

7.1.2 The multiple point calibration involves the measurement of absorbed power over a large range of power settings. Typically, for a 600 W unit, the following power settings are measured; 100,99,98,97, 95,90,80,70,60,50, and 40% using the procedure described in section 7.1.4. This data is clustered about the customary working power ranges. Nonlinearity has been commonly encountered at the upper end of the calibration. If the unit's electronics are known to have nonlinear deviations in any region of proportional power control, it will be necessary to make a set of measurements that bracket the power to be used. The final calibration point should be at the partial power setting that will be used in the test. This setting should be checked periodically to evaluate the integrity of the calibration. If a significant change is detected (±10 W), then the entire calibration should be reevaluated.

7.1.3 The three-point calibration involves the measurement of absorbed power at three different power settings. Measure the power at 100% and 50% using the procedure described in section 7.1.4, and calculate the power setting corresponding to the required power in watts specified in the procedure from the (2-point) line. Measure the absorbed power at that partial power setting. If the measured absorbed power does not correspond to the specified power within ±10 W, use the multiple point calibration in 7.1.2. This point should also be used to periodically verify the integrity of the calibration.

7.1.4 Equilibrate a large volume of water to room temperature (23 ± 2 °C). One kg of reagent water is weighed (1,000.0 g ± 0.1 g) into a fluorocarbon (PFA or TFM) beaker or a beaker made of some other material that does not significantly absorb microwave energy (glass

absorbs microwave energy and is not recommended). The initial temperature of the water should be 23 ± 2 °C measured to ± 0.05 °C. The covered beaker is circulated continuously (in the normal sample path) through the microwave field for 2 minutes at the desired partial power setting with the unit's exhaust fan on maximum (as it will be during normal operation). The beaker is removed and the water vigorously stirred. Use a magnetic stirring bar inserted immediately after microwave irradiation and record the maximum temperature within the first 30 seconds to ± 0.05 °C. Use a new sample for each additional measurement. If the water is reused both the water and the beaker must have returned to 23 ± 2 °C. Three measurements at each power setting should be made.

The absorbed power is determined by the following relationship

$$P = \frac{(K)\ (C_p)\ (m)\ (\Delta T)}{t} \qquad \text{Eq. 1}$$

Where:

P = the apparent power absorbed by the sample in watts (W). (W=joule·sec^{-1})

K = the conversion factor for thermochemical calories·sec^{-1} to watts (=4.184)

C_p = the heat capacity, thermal capacity, or specific heat (cal·g^{-1}·°C^{-1}), of water

m = the mass of the water sample in grams (g)

ΔT = the final temperature minus the initial temperature (°C)

t = the time in seconds (s)

Using the experimental conditions of 2 minutes and 1 kg of distilled water (heat capacity at 25 °C is 0.9997 cal·g^{-1}·°C^{-1}) the calibration equation simplifies to:

$$P = (\Delta T)\ (34.86)$$

NOTE: Stable line voltage is necessary for accurate and reproducible calibration and operation. The line voltage should be within manufacturer's specification, and during measurement and operation not vary by more than ±2 V. A constant power supply may be necessary for microwave use if the source of the line voltage is unstable.

Electronic components in most microwave units are matched to the units' function and output. When any part of the high voltage circuit, power source, or control components in the unit have been serviced or replaced, it will be necessary to recheck the units' calibration power. If the power output has changed significantly (±10 W), then the entire calibration should be reevaluated.

7.2 All digestion vessels and volumetric ware must be carefully acid washed and rinsed with reagent water. When switching between high solids (concentrated) samples and low solids (low concentration) samples all digestion vessels should be cleaned by leaching with hot (1:1) hydrochloric acid (greater than 80°C, but less than boiling) for a minimum of two hours followed with hot (1:1) nitric acid (greater than 80°C, but less than boiling) for a minimum of two hours, rinsed with reagent water, and dried in a clean environment. This cleaning procedure should also be used whenever the prior use of the digestion vessels is unknown or cross contamination from vessels is suspected. Polymeric or glass volumetric ware and storage containers should be cleaned by leaching with more dilute acids (approximately 10% V/V) appropriate for the specific plastics used and then rinsed with reagent water and dried in a clean environment. In addition, to avoid precipitation of silver, ensure that all HCl has been rinsed from the vessels.

7.3 Sample Digestion

7.3.1 Weigh the fluorocarbon (PFA or TFM) digestion vessel, valve and cap assembly to 0.01 g prior to use.

7.3.2 A 45 mL aliquot of a well shaken sample is measured in a graduated cylinder. This aliquot is poured into the digestion vessel with the number of the vessel recorded on the preparation sheet.

7.3.3 A blank sample of reagent water is treated in the same manner along with spikes and duplicates.

7.3.4 Add 5 mL of concentrated nitric acid to each vessel that will be used. Check to make sure the pressure relief disks are in the caps with the smooth side toward the sample and start the caps a few turns on the vessels. Finish tightening the caps in the capping station which will tighten them to a uniform torque pressure of 12 ft-lbs. (16 N-m) or to the manufacturers recommended specifications. Weigh each capped vessel to the nearest 0.01 g.

> CAUTION: Toxic nitrogen oxide fumes may be evolved, therefore all work must be performed in a properly operating ventilation system. The analyst should also be aware of the potential for a vigorous reaction. If a vigorous reaction occurs, allow to cool before capping the vessel.

7.3.5 Evenly distributed the vessels in the carousel according to the manufacturer's recommended specifications. Blanks are treated as samples for the purpose of balancing the power input. When fewer

than the recommended number of samples are digested, the remaining vessels should be filled with 45 mL of reagent water and 5 mL of nitric acid to achieve the full compliment of vessels. This provides an energy balance since the microwave power absorbed is proportional to the total mass in the cavity (Ref. 1).

7.3.6 Program the microwave unit according to the manufacturer's recommended specifications and, if used, connect the pressure vessels to the central overflow vessel with PFA-fluorocarbon tubes. The chosen sequence will bring the samples to 160°C ± 4°C in 10 minutes and will permit a slow rise to 165-170 °C during the second 10 minutes (Ref. 3). Start the turntable motor and be sure the vent fan is running on high and the turntable is turning. Start the microwave generator.

7.3.6.1 Newer microwave units are capable of higher power that permit digestion of a larger number of samples per batch. If the analyst wishes to digest more samples at a time, the analyst may use different power settings as long as they result in the same time and temperature conditions defined in 7.3.6. That is, any sequence of power that brings the samples to 160°C ± 4°C in 10 minutes and permits a slow rise to 165-170°C during the second 10 minutes (Ref. 2).

Issues of safety, structural integrity (both temperature and pressure limitations), heat loss, chemical compatibility, microwave absorption of vessel material, and energy transport will be considerations made in choosing alternative vessels. If all of the considerations are met and the appropriate power settings are provided to reproduce the reaction conditions defined in 7.3.6, then these alternative vessels may be used (Ref. 1,3)

7.3.7 At the end of the microwave program, allow the vessels to cool for at least 5 minutes in the unit before removal to avoid possible injury if a vessel vents immediately after microwave heating. The samples may be cooled outside the unit by removing the carousel and allowing the samples to cool on the bench or in a water bath. When the vessels have cooled to room temperature, weigh and record the weight of each vessel assembly. If the weight of the sample plus acid has decreased by more than 10% discard the sample.

7.3.8 Complete the preparation of the sample by carefully uncapping and venting each vessel in a fume hood. Transfer the sample to an acid-cleaned bottle. If the digested sample contains particulates which may clog nebulizers or interfere with injection of the sample into the instrument, the sample may be centrifuged, allowed to settle or filtered.

7.3.8.1 Centrifugation: Centrifugation at 2,000-3,000 rpm for 10 minutes is usually sufficient to clear the supernatant.

7.3.8.2 Settling: Allow the sample to stand until the supernatant is clear. Allowing a sample to stand overnight will usually accomplish this. If it does not, centrifuge or filter the sample.

7.3.8.3 Filtering: The filtering apparatus must be thoroughly cleaned and prerinsed with dilute (approximately 10% V/V) nitric acid. Filter the sample through qualitative filter paper into a second acid-cleaned container.

7.3.9 The concentration values obtained from analysis must be corrected for the dilution factor from the acid addition. If the sample will be analyzed by ICP-MS additional dilution will generally be necessary. For example, the sample may be diluted by a factor of 20 with reagent water and the acid strength adjusted back to 10% prior to analysis. The dilutions used should be recorded and the measured concentrations adjusted accordingly (e.g., for a 45 mL sample and 5 mL of acid the correction factor is 1.11).

8.0 QUALITY CONTROL

8.1 All quality control measures described in Chapter One, of this Manual, should be followed.

8.2 For each analytical batch of samples processed, analytical reagent blanks (also field blanks if they were taken) should be carried throughout the entire sample preparation and analytical process. These blanks will be useful in determining if samples are being contaminated.

8.3 Duplicate samples should be processed on a routine basis. A duplicate sample is a real sample brought through the whole sample preparation and analytical process. A duplicate sample should be processed with each analytical batch or every 20 samples, whichever is the greater number.

8.4 Spiked samples or standard reference materials should be employed to determine accuracy. A spiked sample should be included with each group of samples processed and whenever a new sample matrix is being analyzed.

9.0 METHOD PERFORMANCE

9.1 Refer to Table 1 for a summary of performance data.

10.0 REFERENCES

1. Introduction to Microwave Sample Preparation: Theory and Practice, Kingston, H. M.; Jassie, L. B., Eds.; ACS Professional Reference Book Series: American Chemical Society, Washington, DC, 1988; Ch 6 & 11.

2. 1985 Annual Book of ASTM Standards, Vol. 11.01; "Standard Specification for Reagent Water"; ASTM: Philadelphia, PA, 1985; D1193-77.

3. Kingston, H. M., Final Report EPA IAG #DWI3932541-01-I, September 30, 1988, Appendix A.

4. Shannon, M., Alternate Test Procedure Application, USEPA Region V, Central Regional Laboratory, 536 S. Clark Street, Chicago, IL 60606, 1989.

5. Kingston, H. M., Walter, P. J., "Comparison of Microwave Versus Conventional Dissolution for Environmental Applications", Spectroscopy, vol. 7 No. 9,20-27,1992.

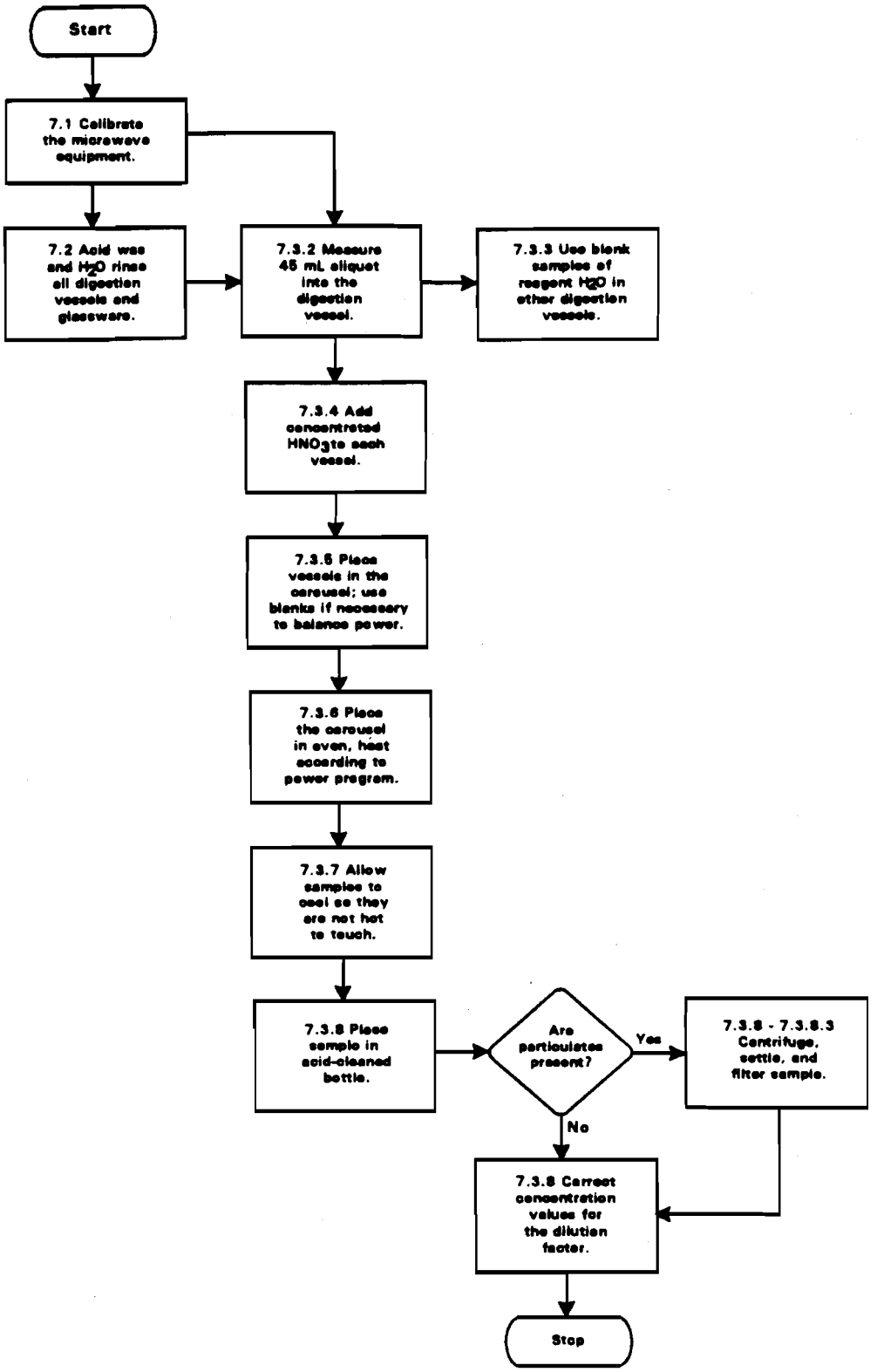
6. Sosinski, P., and Sze C., "Absolute Accuracy Study, Microwave Digestion Method 3015 (Nitric acid only)"; EPA Region III Central Regional Laboratory, 1991.

TABLE 1
MICROWAVE DIGESTION METHOD 3015 (Nitric Acid Only)

Elem	Material	Certified Mean	Observed Mean	Std. Dev.	Relative Standard Deviation	Relative Bias
Al	Tm-11	510.0	485.5	26.3	5.4	-4.80%
Al	Tm-12	2687.0	2770.6	88.2	3.2	3.11%
Al	T-107	220.0	213.5	19.3	9.0	-2.95%
Al	T-109	113.0	117.7	30.6	2.6	4.16%
Ba	Tm-11	450.0	441.4	23.4	5.3	-1.90%
Ba	Tm-12	2529.0	2431.4	70.3	2.9	-3.86%
Ba	T-107	192.0	196.6	15.9	8.1	2.44%
Cd	Tm-11	40.8	44.6	2.1	4.7	9.46%
Cd	Tm-12	237.0	242.3	8	3.3	2.25%
Cd	T-107	14.3	12.4	0.9	7.2	-12.94%
Cd	T-109	12.1	10.3	1.7	16.5	-14.55%
Zn	Tm-11	55.4	55.9	2.6	4.6	1.06%
Zn	Tm-12	314.0	316.5	8.9	2.8	0.82%
Zn	T-107	75.8	81.6	3.3	4.0	7.68%
Zn	T-109	74.0	69.9	4.1	5.8	-5.46%
As	T-107	10.8	12.8	0.84	6.5	19.26%
As	T-109	8.15	90.6	11.0	12.2	11.26%
Co	Tm-11	227.0	242.6	14.1	5.8	6.90%
Co	Tm-12	1067.0	1153.3	35.9	3.1	8.09%
K	T-95	4700.0	5080.3	784	15.4	8.09%
K	T-109	2330.0	2601.5	383.4	14.7	11.65%
Ni	Tm-11	264.0	284.3	16.5	5.8	7.71%
Ni	Tm-12	1234.0	1293.0	39.4	3.0	4.79%
Ni	T-109	57.0	60.8	3.09	5.0	6.72%
Pb	Tm-11	275.0	275.9	32.2	11.7	0.36%
Pb	Tm-12	1326.0	1359.0	35.0	2.6	2.49%
Pb	T-107	26.0	30.0	0.2	0.66	15.65%
Pb	T-109	34.9	39.3	1.2	3.0	12.69%
Sb	WP980-1	16.9	18.3	0.47	2.6	8.27%
Sb	WP980-2	101.5	108.9	34.4	31.6	7.33%
Se	T-95	60.1	65.9	2.6	3.94	9.77%
Se	T-107	11.0	13.0	0.9	6.9	19.00%
Tl	WP980-1	50.0	55.1	2	3.6	10.26%
Tl	WP980-2	6.3	7.0	0.52	7.4	11.66%
V	Tm-11	491.0	532.6	26.1	4.9	8.48%
V	Tm-12	2319.0	2412.8	60.6	2.5	4.05%
Be	T-107	11.0	11.3	0.53	4.7	3.00%
Be	T-109	22.1	25.6	0.91	3.6	15.97%
Ca	T-107	11700.0	12364.0	783.6	6.3	5.68%
Ca	T-109	35400.0	38885.0	999	2.6	9.84%

TABLE 1 (continued)

Elem	Material	Certified Mean	Observed Mean	Std. Dev.	Relative Standard Deviation	Relative Bias
Ca	T-107	11700.0	12364.0	783.6	6.3	5.68%
Ca	T-109	35400.0	38885.0	999	2.6	9.84%
Mg	T-95	32800.0	35002.0	1900	5.4	6.71%
Mg	T-107	2100.0	2246.7	110.5	4.9	6.99%
Mg	T-109	9310.0	10221.7	218.6	2.1	9.79%
Na	T-95	190000.0	218130.0	10700	4.9	14.81%
Na	T-107	20700.0	22528.0	1060	4.7	8.83%
Na	T-109	12000.0	13799.5	516.2	3.7	15.00%
Cr	Tm-11	52.1	64.3	4.1	6.4	23.51%
Cr	Tm-12	299.0	346.0	9.8	2.8	15.74%
Cr	T-107	13.0	22.3	1.5	6.7	71.77%
Cr	T-109	18.7	32.6	6.4	19.6	74.71%
Cu	Tm-11	46.3	76.5	4.4	5.7	65.36%
Cu	Tm-12	288.0	324.0	8.9	2.7	12.52%
Cu	T-107	30.0	42.3	4.0	9.4	41.17%
Cu	T-109	21.4	54.0	3.6	6.7	152.38%
Fe	Tm-11	249.0	289.3	16.4	5.7	16.18%
Fe	Tm-12	1089.0	1182.5	43.5	3.7	8.59%
Fe	T-107	52.0	63.8	8.7	13.6	22.69%
Fe	T-109	106.0	134.0	6.6	4.9	26.50%
Mn	Tm-11	46.0	60.9	3.2	5.2	32.48%
Mn	Tm-12	263.0	304.4	9.1	3.0	15.77%
Mn	T-107	45.0	52.6	3.1	5.9	17.09%
Mn	T-109	34.0	46.6	3.0	6.4	37.18%
Ag	WS378-1	46.0	19.4	5.6	2.9	-57.83%


Start
7.1 Calibrate the microwave equipment.
7.2 Acid wash and H_2O rinse all digestion vessels and glassware.
7.3.2 Measure 45 mL aliquot into the digestion vessel.
7.3.3 Use blank samples of reagent H_2O in other digestion vessels.
7.3.4 Add concentrated HNO_3 to each vessel.
7.3.5 Place vessels in the carousel; use blanks if necessary to balance power.
7.3.6 Place the carousel in oven, heat according to power program.
7.3.7 Allow samples to cool so they are not hot to touch.
7.3.8 Place sample in acid-cleaned bottle.
Are particulates present?
Yes
7.3.8 - 7.3.8.3 Centrifuge, settle, and filter sample.
No
7.3.8 Correct concentration values for the dilution factor.
Stop

METHOD 3020A

ACID DIGESTION OF AQUEOUS SAMPLES AND EXTRACTS FOR TOTAL METALS FOR ANALYSIS BY GFAA SPECTROSCOPY

1.0 SCOPE AND APPLICATION

1.1 This digestion procedure is used for the preparation of aqueous samples, mobility-procedure extracts, and wastes that contain suspended solids for analysis by furnace atomic absorption spectroscopy (GFAA) for the metals listed below. The procedure is used to determine the total amount of the metal in the sample.

1.2 Samples prepared by Method 3020 may be analyzed by GFAA for the following metals:

Beryllium	Lead
Cadmium	Molybdenum
Chromium	Thallium
Cobalt	Vanadium

NOTE: For the digestion and GFAA analysis of arsenic and selenium, see Methods 7060 and 7740. For the digestion and GFAA analysis of silver, see Method 7761.

2.0 SUMMARY OF METHOD

2.1 A mixture of nitric acid and the material to be analyzed is refluxed in a covered Griffin beaker. This step is repeated with additional portions of nitric acid until the digestate is light in color or until its color has stabilized. After the digestate has been brought to a low volume, it is cooled and brought up in dilute nitric acid such that the final dilution contains 3% (v/v) nitric acid. This percentage will vary depending on the amount of acid used to complete the digestion. If the sample contains suspended solids, it must be centrifuged, filtered, or allowed to settle.

3.0 INTERFERENCES

3.1 Interferences are discussed in the referring analytical method.

4.0 APPARATUS AND MATERIALS

4.1 Griffin beakers - 150-mL, or equivalent.

4.2 Watch glasses - ribbed or equivalent.

4.3 Qualitative filter paper or centrifugation equipment.

4.4 Funnel or equivalent.

4.5 Graduated Cylinder - 100mL.

4.6 Electric hot plate or equivalent - adjustable and capable of maintaining a temperature of 90-95°C.

5.0 REAGENTS

5.1 Reagent grade chemicals shall be used in all tests. Unless otherwise indicated, it is intended that all reagents shall conform to the specifications of the Committee on Analytical Reagents of the American Chemical Society, where such specifications are available. Other grades may be used, provided it is first ascertained that the reagent is of sufficiently high purity to permit its use without lessening the accuracy of the determination.

5.2 Reagent Water. Reagent water will be interference free. All references to water in the method refer to reagent water unless otherwise specified. Refer to Chapter One for a definition of reagent water.

5.3 Nitric acid (concentrated), HNO_3. Acid should be analyzed to determine levels of impurities. If method blank is < MDL, the acid can be used.

6.0 SAMPLE COLLECTION, PRESERVATION, AND HANDLING

6.1 All samples must have been collected using a sampling plan that addresses the considerations discussed in Chapter Nine of this manual.

6.2 All sample containers must be prewashed with detergents, acids, and water. Plastic and glass containers are both suitable. See Chapter Three, Step 3.1.3, for further information.

6.3 Aqueous wastewaters must be acidified to a pH of < 2 with HNO_3.

7.0 PROCEDURE

7.1 Transfer a 100-mL representative aliquot of the well-mixed sample to a 150-mL Griffin beaker and add 3 mL of concentrated HNO_3. Cover the beaker with a ribbed watch glass. Place the beaker on a hot plate and cautiously evaporate to a low volume (5 mL), making certain that the sample does not boil and that no portion of the bottom of the beaker is allowed to go dry. Cool the beaker and add another 3-mL portion of concentrated HNO_3. Cover the beaker with a non-ribbed watch glass and return to the hot plate. Increase the temperature of the hot plate so that a gentle reflux action occurs.

7.2 Continue heating, adding additional acid as necessary, until the digestion is complete (generally indicated when the digestate is light in color or does not change in appearance with continued refluxing). When the digestion is complete, evaporate to a low volume (3 mL); use a ribbed watch glass, not allowing any portion of the bottom of the beaker to go dry. Remove the beaker and add approximately 10 mL of water, mix, and continue warming the beaker for 10 to 15 minutes to allow additional solubilization of any residue to occur.

7.3 Remove the beaker from the hot plate and wash down the beaker walls and watch glass with water. When necessary, filter or centrifuge the sample to remove silicates and other insoluble material that may interfere with injecting the sample into the graphite atomizer. (This additional step can cause sample contamination unless the filter and filtering apparatus are thoroughly cleaned and prerinsed with dilute HNO_3.) Adjust to the final volume of 100 mL with water. The sample is now ready for analysis.

8.0 QUALITY CONTROL

8.1 All quality control measures described in Chapter One should be followed.

8.2 For each batch of samples processed, method blanks should be carried throughout the entire sample preparation and analytical process. These blanks will be useful in determining if samples are being contaminated. Refer to Chapter One for the proper protocol when analyzing blanks.

8.3 Replicate samples should be processed on a routine basis. Replicate samples will be used to determine precision. The sample load will dictate frequency, but 5% is recommended. Refer to Chapter One for the proper protocol when analyzing replicates.

8.4 Spiked samples or standard reference materials should be employed to determine accuracy. A spiked sample should be included with each batch of samples processed or 5% and whenever a new sample matrix is being analyzed. Refer to Chapter One for the proper protocol when analyzing spikes.

8.5 The concentration of all calibration standards should be verified against a quality control check sample obtained from an outside source. Refer to Chapter One for the proper protocol.

8.6 The method of standard addition shall be used for the analysis of all EP extracts. See Method 7000, Step 8.7, for further information.

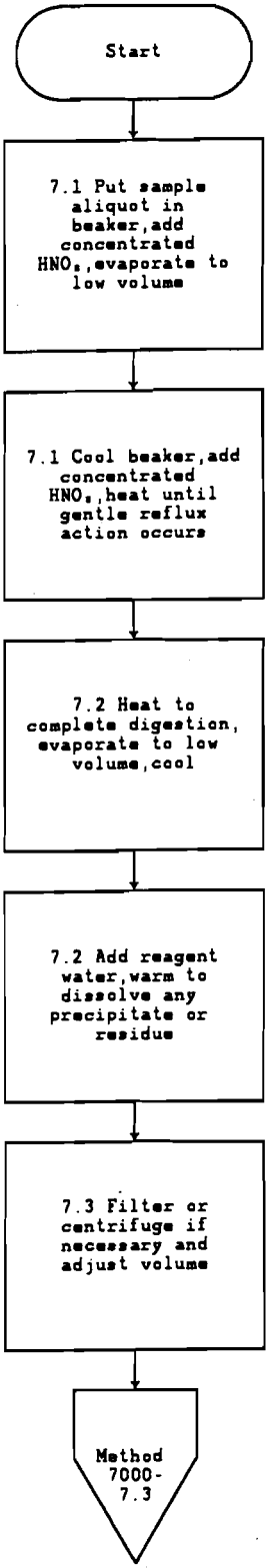
9.0 METHOD PERFORMANCE

9.1 No data provided.

10.0 REFERENCES

1. Rohrbough, W.G.; et al. Reagent Chemicals, American Chemical Society Specifications, 7th ed.; American Chemical Society: Washington, DC, 1986.

2. 1985 Annual Book of ASTM Standards, Vol. 11.01; "Standard Specification for Reagent Water"; ASTM: Philadelphia, PA, 1985; D1193-77.


Start
7.1 Put sample aliquot in beaker, add concentrated HNO_3, evaporate to low volume
7.1 Cool beaker, add concentrated HNO_3, heat until gentle reflux action occurs
7.2 Heat to complete digestion, evaporate to low volume, cool
7.2 Add reagent water, warm to dissolve any precipitate or residue
7.3 Filter or centrifuge if necessary and adjust volume
Method 7000-7.3

METHOD 3040

DISSOLUTION PROCEDURE FOR OILS, GREASES, OR WAXES

1.0 SCOPE AND APPLICATION

1.1 Method 3040 is used for the preparation of samples containing oils, greases, or waxes for analysis by atomic absorption spectroscopy (AAS) or inductively coupled argon plasma emission spectroscopy (ICP) for the following metals:

Antimony	Iron
Beryllium	Manganese
Cadmium	Nickel
Chromium	Vanadium
Copper	

1.2 This method is a solvent dissolution procedure, not a digestion procedure. This procedure can be very useful in the analysis of crude oil, but with spent or used oil high in particulate material it is less effective; most particulate material is not dissolved, and therefore the analysis is not a "total" metal determination. Because the highest percentage of metals is expected to be contained in the particulate material, oil analysis using Method 3040 will not provide an adequate estimate of the total metals concentration.

2.0 SUMMARY OF METHOD

2.1 A representative sample is dissolved in an appropriate solvent (e.g., xylene or methyl isobutyl ketone). Organometallic standards are prepared using the same solvent, and the samples and standards are analyzed by AAS or ICP.

3.0 INTERFERENCES

3.1 Diluted samples and diluted organometallic standards are often unstable. Once standards and samples are diluted, they should be analyzed as soon as possible.

3.2 Solvent blanks should be used to rinse nebulizers thoroughly following aspiration of high concentration standards or samples.

3.3 Viscosity differences can result in different rates of sample introduction; therefore, all analyses shall be performed by the method of standard addition. Peristaltic pumps often prove useful when analysis is performed by ICP.

4.0 APPARATUS AND MATERIALS

4.1 Volumetric glassware.

4.2 Balance.

4.3 Atomic absorption spectrometer: With an auxiliary oxidant control and a mechanism for background correction.

4.4 Inductively coupled argon plasma emission spectrometer system: With a mechanism for background correction and interelement interference correction. A peristaltic pump is optional.

5.0 REAGENTS

5.1 Methyl isobutyl ketone (MIBK).

5.2 Xylene.

5.3 Organometallic standards (two possible sources are Conostan Division, Conoco Speciality Products, Inc., P.O. Box 1267, Ponca City, OK 74601, and the U.S. Department of Commerce, National Bureau of Standards, Washington, DC 20234).

6.0 SAMPLE COLLECTION, PRESERVATION, AND HANDLING

6.1 All samples must have been collected using a sampling plan that addresses the considerations discussed in Chapter Nine of this manual.

6.2 Samples shall be stored in an undiluted state at room temperature.

6.3 Samples should be processed and analyzed as soon as possible.

7.0 PROCEDURE

7.1 Weigh out a 2-g representative sample of the waste or extract. Separate and weigh the phases if more than one phase is present.

7.2 Weigh an aliquot of the organic phase and dilute the aliquot in the appropriate solvent. Warming facilitates the subsampling of crude-type oils and greases and wax-type wastes. Xylene is usually the preferred solvent for longer-chain hydrocarbons and for most analyses performed by ICP. The longer-chain hydrocarbons usually require a minimum of a 1:10 dilution, and lighter oils may require only a 1:5 dilution if low detection limits are required.

7.3 All metals must be analyzed by the method of standard additions. Because the method of standard additions can account only for multiplicative interferences (matrix or physical interferences), the analytical program must

account for additive interference (nonspecific absorption and scattering in AAS and nonspecific emission and interelement interference in ICP) by employing background correction.

7.4 Sample preparation for the method of standard additions can be performed on a weight or volume basis. Sample aliquots of viscous wastes should be weighed. Weigh identical amounts of the sample into three wide-mouth vials. Dilute the first vial such that the final concentration falls on the lower end of the linear portion of the calibration curve and significantly above the detection limit. Add sufficient standard to the second aliquot to increase the sample concentration by approximately 50%. Adjust the third sample concentration so that it is approximately twice that of the first. The second and third aliquots are then diluted to the same final volume as the first aliquot.

7.5 Set up and calibrate the analytical instrumentation according to the manufacturer's directions for nonaqueous samples.

7.6 Report data as the weighted average for all sample phases.

8.0 QUALITY CONTROL

8.1 Preparation blanks (e.g., Conostan base oil or mineral oil plus reagents) should be carried through the complete sample-preparation and analytical process on a routine basis. These blanks will be useful in detecting and determining the magnitude of any sample contamination.

8.2 Duplicate samples should be processed on a routine basis. Duplicate samples will be used to determine precision. The sample load will dictate the frequency, but 20% is recommended.

8.3 Samples and standards should be diluted as closely as possible to the time of analysis.

8.4 All analyses must be performed by the method of standard additions. See Method 7000, Section 8.7, for further information.

8.5 Data must be corrected for background absorption and emission and interelement interferences.

9.0 METHOD PERFORMANCE

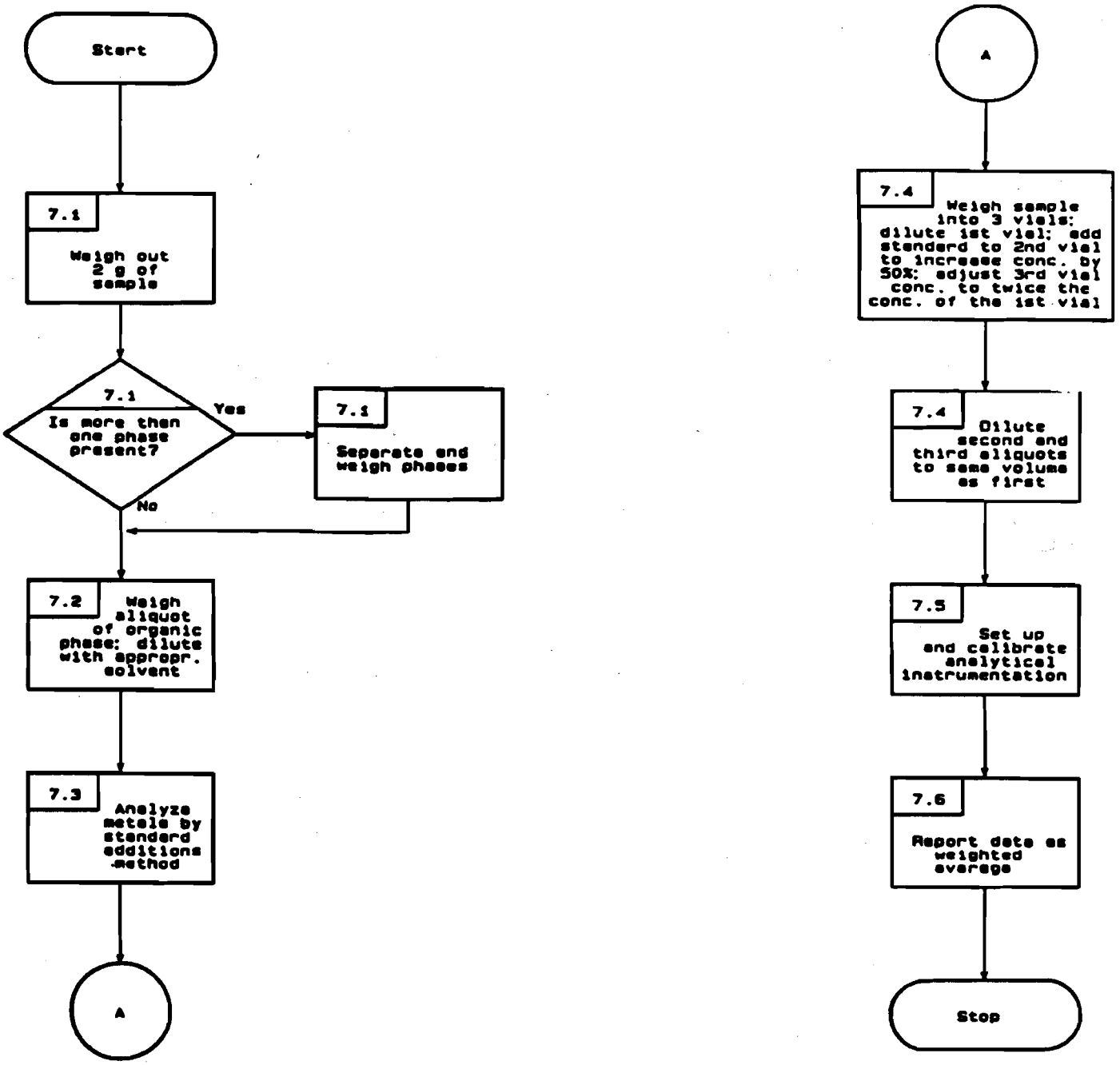
9.1 No data provided.

10.0 REFERENCES

10.1 None required.

METHOD 3040

DISSOLUTION PROCEDURE FOR OILS, GREASE, OR WAXES



Revision 0
Date September 1986

METHOD 3050A

ACID DIGESTION OF SEDIMENTS, SLUDGES, AND SOILS

1.0 SCOPE AND APPLICATION

1.1 This method is an acid digestion procedure used to prepare sediments, sludges, and soil samples for analysis by flame or furnace atomic absorption spectroscopy (FLAA and GFAA, respectively) or by inductively coupled argon plasma spectroscopy (ICP). Samples prepared by this method may be analyzed by ICP for all the listed metals, or by FLAA or GFAA as indicated below (see also Step 2.1):

FLAA		GFAA
Aluminum	Magnesium	Arsenic
Barium	Manganese	Beryllium
Beryllium	Molybdenum	Cadmium
Cadmium	Nickel	Chromium
Calcium	Osmium	Cobalt
Chromium	Potassium	Iron
Cobalt	Silver	Lead
Copper	Sodium	Molybdenum
Iron	Thallium	Selenium
Lead	Vanadium	Thallium
	Zinc	Vanadium

NOTE: See Method 7760 for FLAA preparation for Silver.

2.0 SUMMARY OF METHOD

2.1 A representative 1- to 2-g (wet weight) sample is digested in nitric acid and hydrogen peroxide. The digestate is then refluxed with either nitric acid or hydrochloric acid. Hydrochloric acid is used for flame AA and ICP analyses and nitric acid is used for furnace AA work. Dilute hydrochloric acid is used as the final reflux acid for (1) the ICP analysis of As and Se, and (2) the flame AA or ICP analysis of Ag, Al, Ba, Be, Ca, Cd, Co, Cr, Cu, Fe, K, Mg, Mn, Mo, Na, Ni, Os, Pb, Tl, V, and Zn. Dilute nitric acid is employed as the final dilution acid for the furnace AA analysis of As, Be, Cd, Cr, Co, Fe, Pb, Mo, Se, Tl, and V. The diluted samples have an approximate acid concentration of 5.0% (v/v). A separate sample shall be dried for a total % solids determination.

3.0 INTERFERENCES

3.1 Sludge samples can contain diverse matrix types, each of which may present its own analytical challenge. Spiked samples and any relevant standard reference material should be processed to aid in determining whether Method 3050 is applicable to a given waste.

4.0 APPARATUS AND MATERIALS

4.1 Conical Phillips beakers - 250-mL, or equivalent.

4.2 Watch glasses ribbed or equivalent.

4.3 Drying ovens - That can be maintained at 30° C.

4.4 Thermometer - That covers range of 0-200°C.

4.5 Filter paper - Whatman No. 41 or equivalent.

4.6 Centrifuge and centrifuge tubes.

4.7 Analytical Balance - Capable of accurately weighing to the nearest 0.01 g.

4.8 Electric Hot Plate or equivalent - Adjustable and capable of maintaining a temperature of 90-95°C.

4.9 Glass Funnel or equivalent.

4.10 Graduated cylinder or equivalent.

5.0 REAGENTS

5.1 Reagent grade chemicals shall be used in all tests. Unless otherwise indicated, it is intended that all reagents shall conform to the specifications of the Committee on Analytical Reagents of the American Chemical Society, where such specifications are available. Other grades may be used, provided it is first ascertained that the reagent is of sufficiently high purity to permit its use without lessening the accuracy of the determination. If the purity of a reagent is questionable, analyze the reagent to determine the level of impurities. The reagent blank must be less than the MDL in order to be used.

5.2 Reagent Water. Reagent water will be interference free. All references to water in the method refer to reagent water unless otherwise specified. Refer to Chapter One for a definition of reagent water.

5.3 Nitric acid (concentrated), HNO_3. Acid should be analyzed to determine level of impurities. If method blank is < MDL, the acid can be used.

5.4 Hydrochloric acid (concentrated), HCl. Acid should be analyzed to determine level of impurities. If method blank is < MDL, the acid can be used.

5.4 Hydrogen peroxide (30%), H_2O_2. Oxidant should be analyzed to determine level of impurities.

6.0 SAMPLE COLLECTION, PRESERVATION, AND HANDLING

6.1 All samples must have been collected using a sampling plan that addresses the considerations discussed in Chapter Nine of this manual.

6.2 All sample containers must be prewashed with detergents, acids, and water. Plastic and glass containers are both suitable. See Chapter Three, Step 3.1.3, for further information.

6.3 Nonaqueous samples shall be refrigerated upon receipt and analyzed as soon as possible.

7.0 PROCEDURE

7.1 Mix the sample thoroughly to achieve homogeneity. For each digestion procedure, weigh to the nearest 0.01 g and transfer to a conical beaker 1.00-2.00 g of sample. For samples with low percent solids a larger sample size may be used as long as digestion is completed.

7.2 Add 10 mL of 1:1 HNO_3, mix the slurry, and cover with a watch glass. Heat the sample to 95°C and reflux for 10 to 15 minutes without boiling. Allow the sample to cool, add 5 mL of concentrated HNO_3, replace the watch glass, and reflux for 30 minutes. Repeat this last step to ensure complete oxidation. Using a ribbed watch glass, allow the solution to evaporate to 5 mL without boiling, while maintaining a covering of solution over the bottom of the beaker.

7.3 After Step 7.2 has been completed and the sample has cooled, add 2 mL of water and 3 mL of 30% H_2O_2. Cover the beaker with a watch glass and return the covered beaker to the hot plate for warming and to start the peroxide reaction. Care must be taken to ensure that losses do not occur due to excessively vigorous effervescence. Heat until effervescence subsides and cool the beaker.

7.4 Continue to add 30% H_2O_2 in 1-mL aliquots with warming until the effervescence is minimal or until the general sample appearance is unchanged.

NOTE: Do not add more than a total of 10 mL 30% H_2O_2.

7.5 If the sample is being prepared for (a) the **ICP analysis** of As and Se, or (b) the **flame AA or ICP analysis** of Ag, Al, Ba, Be, Ca, Cd, Co, Cr, Cu, Fe, K, Mg, Mn, Mo, Na, Ni, Os, Pb, Tl, V, and Zn, then add 5 mL of concentrated HCl and 10 mL of water, return the covered beaker to the hot plate, and reflux for an additional 15 minutes without boiling. After cooling, dilute to a 100 mL volume with water. Particulates in the digestate that may clog the nebulizer should be removed by filtration, by centrifugation, or by allowing the sample to settle.

7.5.1 Filtration - Filter through Whatman No. 41 filter paper (or equivalent).

7.5.2 Centrifugation - Centrifugation at 2,000-3,000 rpm for 10 minutes is usually sufficient to clear the supernatant.

7.5.3 The diluted sample has an approximate acid concentration of 5.0% (v/v) HCl and 5.0% (v/v) HNO_3. The sample is now ready for analysis.

7.6 If the sample is being prepared for the furnace analysis of As, Be, Cd, Co, Cr, Fe, Mo, Pb, Se, Tl, and V, cover the sample with a ribbed watch glass and continue heating the acid-peroxide digestate until the volume has been reduced to approximately 5 mL. After cooling, dilute to 100 mL with water. Particulates in the digestate should then be removed by filtration, by centrifugation, or by allowing the sample to settle.

7.6.1 Filtration - Filter through Whatman No. 41 filter paper (or equivalent).

7.6.2 Centrifugation - Centrifugation at 2,000-3,000 rpm for 10 minutes is usually sufficient to clear the supernatant.

7.6.3 The diluted digestate solution contains approximately 5% (v/v) HNO_3. For analysis, withdraw aliquots of appropriate volume and add any required reagent or matrix modifier. The sample is now ready for analysis.

7.7 Calculations

7.7.1 The concentrations determined are to be reported on the basis of the actual weight of the sample. If a dry weight analysis is desired, then the percent solids of the sample must also be provided.

7.7.2 If percent solids is desired, a separate determination of percent solids must be performed on a homogeneous aliquot of the sample.

8.0 QUALITY CONTROL

8.1 All quality control measures described in Chapter One should be followed.

8.2 For each batch of samples processed, preparation blanks should be carried throughout the entire sample preparation and analytical process. These blanks will be useful in determining if samples are being contaminated. Refer to Chapter One for the proper protocol when analyzing blanks.

8.3 Replicate samples should be processed on a routine basis. Replicate samples will be used to determine precision. The sample load will dictate frequency, but 5% is recommended. Refer to Chapter One for the proper protocol when analyzing replicates.

8.4 Spiked samples or standard reference materials must be employed to determine accuracy. A spiked sample should be included with each batch of

samples processed and whenever a new sample matrix is being analyzed. Refer to Chapter One for the proper protocol when analyzing spikes.

8.5 The concentration of all calibration standards should be verified against a quality control check sample obtained from an outside source.

9.0 METHOD PERFORMANCE

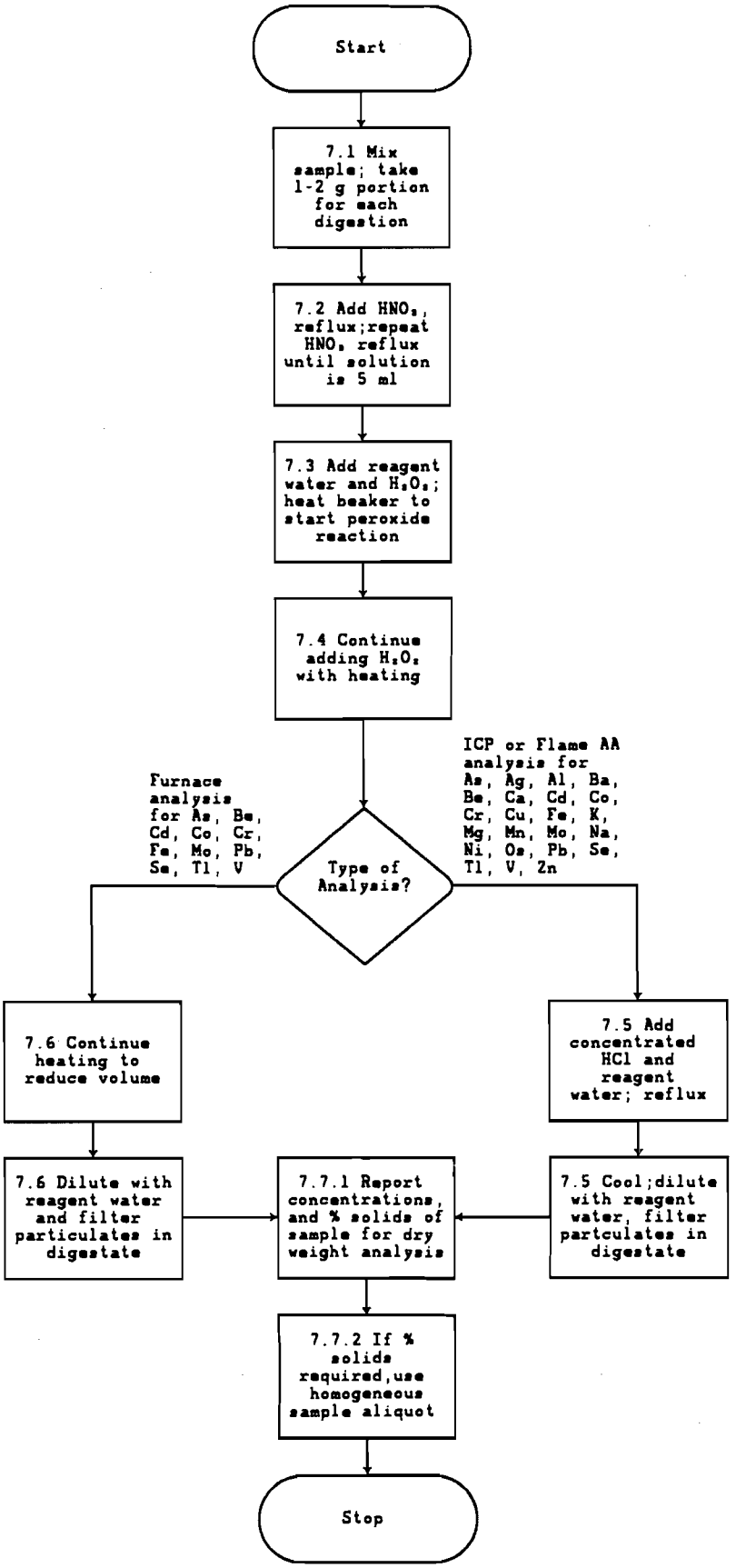
9.1 No data provided.

10.0 REFERENCES

1. Rohrbough, W.G.; et al. Reagent Chemicals, American Chemical Society Specifications, 7th ed.; American Chemical Society: Washington, DC, 1986.

2. 1985 Annual Book of ASTM Standards, Vol. 11.01; "Standard Specification for Reagent Water"; ASTM: Philadelphia, PA, 1985; D1193-77.

3. Edgell, K.; USEPA Method Study 37 - SW-846 Method 3050 Acid Digestion of Sediments, Sludges, and Soils. EPA Contract No. 68-03-3254, November 1988.


Start
7.1 Mix sample; take 1-2 g portion for each digestion
7.2 Add HNO_3, reflux;repeat HNO_3, reflux until solution is 5 ml
7.3 Add reagent water and H_2O_2; heat beaker to start peroxide reaction
7.4 Continue adding H_2O_2 with heating
Type of Analysis?
Furnace analysis for As, Be, Cd, Co, Cr, Fe, Mo, Pb, Se, Tl, V
ICP or Flame AA analysis for As, Ag, Al, Ba, Be, Ca, Cd, Co, Cr, Cu, Fe, K, Mg, Mn, Mo, Na, Ni, Os, Pb, Se, Tl, V, Zn
7.6 Continue heating to reduce volume
7.5 Add concentrated HCl and reagent water; reflux
7.6 Dilute with reagent water and filter particulates in digestate
7.7.1 Report concentrations, and % solids of sample for dry weight analysis
7.5 Cool;dilute with reagent water, filter particulates in digestate
7.7.2 If % solids required,use homogeneous sample aliquot
Stop

METHOD 3051

MICROWAVE ASSISTED ACID DIGESTION OF SEDIMENTS, SLUDGES, SOILS, AND OILS

1.0 SCOPE AND APPLICATION

1.1 This method is applicable to the microwave assisted acid digestion of sludges, sediments, soils, and oils for the following elements:

Aluminum	Cadmium	Iron	Molybdenum	Sodium
Antimony	Calcium	Lead	Nickel	Strontium
Arsenic	Chromium	Magnesium	Potassium	Thallium
Boron	Cobalt	Manganese	Selenium	Vanadium
Barium	Copper	Mercury	Silver	Zinc
Beryllium				

1.2 This method is provided as an alternative to Method 3050. It is intended to provide a rapid multielement acid leach digestion prior to analysis so that decisions can be made about site cleanup levels, the need for TCLP testing of a waste and whether a BDAT process is providing acceptable performance. If a decomposition including hydrochloric acid is required for certain elements, it is recommended that Method 3050A be used. Digests produced by the method are suitable for analysis by flame atomic absorption (FLAA), graphite furnace atomic absorption (GFAA), inductively coupled plasma emission spectroscopy (ICP-ES) and inductively coupled plasma mass spectrometry (ICP-MS). Due to the rapid advances in microwave technology, consult your manufacturer's recommended instructions for guidance on their microwave digestion system and refer to the SW-846 "DISCLAIMER" when conducting analyses using Method 3051.

2.0 SUMMARY OF METHOD

2.1 A representative sample of up to 0.5 g is digested in 10 mL of concentrated nitric acid for 10 min using microwave heating with a suitable laboratory microwave unit. The sample and acid are placed in a fluorocarbon (PFA or TFM) microwave vessel. The vessel is capped and heated in the microwave unit. After cooling, the vessel contents are filtered, centrifuged, or allowed to settle and then diluted to volume and analyzed by the appropriate SW-846 method (Ref. 1).

3.0 INTERFERENCES

3.1 Very reactive or volatile materials that may create high pressures when heated may cause venting of the vessels with potential loss of sample and analytes. The complete decomposition of either carbonates, or carbon based samples, may cause enough pressure to vent the vessel if the sample size is greater than 0.25 g when used in the 120 mL vessels with a pressure relief device that has an upper limit of 7.5± 0.7 atm (110 ± 10 psi).

4.0 APPARATUS AND MATERIALS

4.1 Microwave apparatus requirements.

4.1.1 The microwave unit provides programmable power with a minimum of 574 W, which can be programmed to within ± 10 W of the required power. Typical units provide a nominal 600 W to 1200 W of power. Pressure, or especially temperature, monitoring and control of the microwave unit are desirable.

4.1.2 The microwave unit cavity is corrosion resistant and well ventilated.

4.1.3 All electronics are protected against corrosion for safe operation.

4.1.4 The system requires fluorocarbon (PFA or TFM) digestion vessels (120 mL capacity) capable of withstanding pressures up to 7.5 ± 0.7 atm (110 ± 10 psi) and capable of controlled pressure relief at pressures exceeding 7.5 ± 0.7 atm (110 ± 10 psi).

4.1.5 A rotating turntable is employed to insure homogeneous distribution of microwave radiation within the unit. The speed of the turntable should be a minimum of 3 rpm.

> CAUTION: Those laboratories now using or contemplating the use of kitchen type microwave ovens for this method should be aware of several signifant safety issues. First, when an acid such as nitric is used to assist sample digestion in microwave units in open vessels, or sealed vesselsequippedres, there is the potential for the acid gases released to corrode the safety devices that prevent the microwave magnetron from shutting off when the door is opened. This can result in operator exposure to microwave energy. Use of a unit with corrosion resistant safety devices prevents this from occurring.
>
> CAUTION: The second safety concern relates to the use of sealed containers without pressure relief valves in the unit. Temperature is the important variable controlling the reaction. Pressure is needed to attain elevated temperatures but must be safely contained. However, many digestion vessels constructed from certain fluorocarbons may crack, burst, or explode in the unit under certain pressures. Only unlined fluorocarbon (PFA or TFM) containers with pressure relief mecahnisms or containers with PFA-fluorocarbon liners and pressure relief mechanisms are considered acceptable at present.
>
> Users are therefore advised not to use kitchen type microwave ovens or to use sealed containers without pressure relief

valves for microwave acid digestions by this method. Use of laboratory-grade microwave equipment is required to prevent safety hazards. For further details consult reference 2.

CAUTION: There are many safety and operational recommendations specific to the model and manufacturer of the microwave equipment used in individual laboratories. These specific suggestions are beyond the scope of this method and require the analyst to consult the specific equipment manual, manufacturer and literature for proper and safe operation of the microwave equipment and vessels.

4.2 Volumetric graduated cylinder, 50 or 100 mL capacity or equivalent.

4.3 Filter paper, qualitative or equivalent.

4.4 Filter funnel, glass or disposable polypropylene.

4.5 Analytical balance, 300 g capacity, and minimum ± 0.01 g.

5.0 REAGENTS

5.1 All acids should be sub-boiling distilled where possible to minimize the blank levels due to metallic contamination. Other grades may be used, provided it is first ascertained that the reagent is of sufficient purity to permit its use without lessening the accuracy of the determination. If the purity of a reagent is questionable, analyze the reagent to determine the level of impurities. The reagent blank must be less than the MDL in order to be used.

5.1.1 Concentrated nitric acid, HNO_3. Acid should be analyzed to determine levels of impurity. If the method blank is less than the MDL, the acid can be used.

5.2 Reagent Water. Reagent water shall be interference free. All references to water in the method refer to reagent water unless otherwise specified (Ref. 3).

6.0 SAMPLE COLLECTION, PRESERVATION, AND HANDLING

6.1 All samples must have been collected using a sampling plan that addresses the considerations discussed in Chapter Nine of this manual.

6.2 All sample containers must be prewashed with detergents, acids and water. Plastic and glass containers are both suitable. See Chapter Three, sec. 3.1.3 of this manual, for further information.

6.3 Samples must be refrigerated upon receipt and analyzed as soon as possible.

7.0 PROCEDURE

7.1 Calibration of Microwave Equipment

NOTE: If the microwave unit uses temperature feedback control capable of replicating the performance specifications of the method, then the calibration procedure may be omitted.

7.1.1 Measurement of the available power for heating is evaluated so that absolute power in watts may be transferred from one microwave unit to another. For cavity type microwave equipment, this is accomplished by measuring the temperature rise in 1 kg of water exposed to microwave radiation for a fixed period of time. The analyst can relate power in watts to the partial power setting of the unit. The calibration format required for laboratory microwave units depends on the type of electronic system used by the manufacturer to provide partial microwave power. Few units have an accurate and precise linear relationship between percent power settings and absorbed power. Where linear circuits have been utilized, the calibration curve can be determined by a three-point calibration method (7.1.3), otherwise, the analyst must use the multiple point calibration method (7.1.2).

7.1.2 The multiple point calibration involves the measurement of absorbed power over a large range of power settings. Typically, for a 600 W unit, the following power settings are measured; 100, 99, 98, 97, 95, 90, 80, 70, 60, 50, and 40% using the procedure described in section 7.1.4. This data is clustered about the customary working power ranges. Nonlinearity has been commonly encountered at the upper end of the calibration. If the unit's electronics are known to have nonlinear deviations in any region of proportional power control, it will be necessary to make a set of measurements that bracket the power to be used. The final calibration point should be at the partial power setting that will be used in the test. This setting should be checked periodically to evaluate the integrity of the calibration. If a significant change is detected (±10 W), then the entire calibration should be reevaluated.

7.1.3 The three-point calibration involves the measurement of absorbed power at three different power settings. Measure the power at 100% and 50% using athe procedure described in section 7.1.4. From the 2-point line calculate the power setting corresponding to the required power in watts specified in the procedure. Measure the absorbed power at that partial power setting. If the measured absorbed power does not correspond to the specified power within ±10 W, use the multiple point calibration in 7.1.2. This point should also be used to periodically verify the integrity of the calibration.

7.1.4 Equilibrate a large volume of water to room temperature (23 ± 2°C). One kg of reagent water is weighed (1,000.0 g ± 0.1 g) into a fluorocarbon beaker or a beaker made of some other material that does not significantly absorb microwave energy (glass absorbs microwave energy and is not recommended). The initial temperature of the water should be

23 ± 2°C measured to ± 0.05°C. The covered beaker is circulated continuously (in the normal sample path) through the microwave field for 2 minutes at the desired partial power setting with the unit's exhaust fan on maximum (as it will be during normal operation). The beaker is removed and the water vigorously stirred. Use a magnetic stirring bar inserted immediately after microwave irradiation and record the maximum temperature within the first 30 seconds to ± 0.05°C. Use a new sample for each additional measurement. If the water is reused both the water and the beaker must have returned to 23 ± 2°C. Three measurements at each power setting should be made.

The absorbed power is determined by the following relationship:

Eq. 1
$$P = \frac{(K)\ (C_p)\ (m)\ (\Delta T)}{t}$$

Where:

P = the apparent power absorbed by the sample in watts (W) (W=joule·sec^{-1})

K = the conversion factor for thermochemical calories·sec^{-1} to watts (=4.184)

C_p = the heat capacity, thermal capacity, or specific heat (cal·g^{-1}·°C^{-1}) of water

m = the mass of the water sample in grams (g)

ΔT = the final temperature minus the initial temperature (°C)

t = the time in seconds (s)

Using the experimental conditions of 2 minutes and 1 kg of distilled water (heat capacity at 25 °C is 0.9997 cal·g^{-1}·°C^{-1}) the calibration equation simplifies to:

Eq. 2
$$P = (\Delta T)\ (34.86)$$

NOTE: Stable line voltage is necessary for accurate and reproducible calibration and operation. The line voltage should be within manufacturer's specification, and during measurement and operation should not vary by more than ±2 V. A constant power supply may be necessary for microwave use if the source of the line voltage is unstable.

Electronic components in most microwave units are matched to the units' function and output. When any part of the high voltage

circuit, power source, or control components in the unit have been serviced or replaced, it will be necessary to recheck the units' calibration. If the power output has changed significantly (±10 W), then the entire calibration should be reevaluated.

7.2 All digestion vessels and volumetric ware must be carefully acid washed and rinsed with reagent water. When switching between high concentration samples and low concentration samples, all digestion vessels should be cleaned by leaching with hot (1:1) hydrochloric acid (greater than 80°C, but less than boiling) for a minimum of two hours followed with hot (1:1) nitric acid (greater than 80°C, but less than boiling) for a minimum of two hours and rinsed with reagent water and dried in a clean environment. This cleaning procedure should also be used whenever the prior use of the digestion vessels is unknown or cross contamination from vessels is suspected. Polymeric or glass volumetric ware and storage containers should be cleaned by leaching with more dilute acids (approximately 10% V/V) appropriate for the specific plastics used and then rinsed with reagent water and dried in a clean environment. To avoid precipitation of silver, ensure that all HCl has been rinsed from the vessels.

7.3 Sample Digestion

7.3.1 Weigh the fluorocarbon (PFA or TFM) digestion vessel, valve and capassembly to 0.001 g prior to use.

7.3.2 Weigh a well-mixed sample to the nearest 0.001 g into the fluorocarbon sample vessel equipped with a single-ported cap and a pressure relief valve. For soils, sediments, and sludges use no more than 0.500 g. For oils use no more than 0.250 g.

7.3.3 Add 10 ± 0.1 mL concentrated nitric acid in a fume hood. If a vigorous reaction occurs, allow the reaction to stop before capping the vessel. Cap the vessel and torque the cap to 12 ft-lbs (16 N-m) or according to the unit manufacturer's directions. Weigh the vessels to the nearest 0.001 g. Place the vessels in the microwave carousel.

CAUTION: Toxic nitrogen oxide fumes may be evolved, therefore all work must be performed in a properly operating ventilation system. The analyst should also be aware of the potential for a vigorous reaction. If a vigorous reaction occurs, allow to cool before capping the vessel.

CAUTION: When digesting samples containing volatile or easily oxidized organic compounds, initially weigh no more than 0.10 g and observe the reaction before capping the vessel. If a vigorous reaction occurs, allow the reaction to cease before capping the vessel. If no appreciable reaction occurs, a sample weight up to 0.25 g can be used.

CAUTION: All samples known or suspected of containing more than 5-10% organic material should be predigested in a hood for at least 15 minutes.

7.3.4 Properly place the carousel in the microwave unit according to the manufacturer's recommended specifications and, if used, connect the pressure vessels to the central overflow vessel with PFA-fluorocarbon tubes. Any vessels containing 10 mL of nitric acid for analytical blank purposes are counted as sample vessels. When fewer than the recommended number of samples are to be digested, the remaining vessels should be filled with 10 mL of nitric acid to achieve the full complement of vessels. This provides an energy balance since the microwave power absorbed is proportional to the total mass in the cavity (Ref. 4). Irradiate each group of sample vessels for 10 minutes. The temperature of each sample should rise to 175 °C in less than 5.5 minutes and remain between 170-180 °C for the balance of the 10 minute irradiation period. The pressure should peak at less than 6 atm for most soil, sludge, and sediment samples (Ref. 5). The pressure will exceed these limits in the case of high concentrations of carbonate or organic compounds. In these cases the pressure will be limited by the relief pressure of the vessel to 7.5 ± 0.7 atm (110 ± 10 psi). All vessels should be sealed according to the manufacturers recommended specifications.

7.3.4.1 Newer microwave units are capable of higher power (W) that permits digestion of a larger number of samples per batch. If the analyst wishes to digest more samples at a time, the analyst may use different values of power as long as they result in the same time and temperature conditions defined in 7.3.4. That is, any sequence of power that brings the samples to 175°C in 5.5 minutes and permits a slow rise to 175 - 180°C during the remaining 4.5 minutes (Ref. 5).

Issues of safety, structural integrity (both temperature and pressure limitations), heat loss, chemical compatibility, microwave absorption of vessel material, and energy transport will be considerations made in choosing alternative vessels. If all of the considerations are met and the appropriate power settings provided to reproduce the reaction conditions defined in 7.3.4, then these alternative vessels may be used (Ref. 1,2).

7.3.5 At the end of the microwave program, allow the vessels to cool for a minimum of 5 minutes before removing them from the microwave unit. When the vessels have cooled to room temperature, weigh and record the weight of each vessel assembly. If the weight of acid plus sample has decreased by more than 10 percent from the original weight, discard the sample. Determine the reason for the weight loss. These are typically attributed to loss of vessel seal integrity, use of a digestion time longer than 10 minutes, too large a sample, or improper heating conditions. Once the source of the loss has been corrected, prepare a new sample or set of samples for digestion beginning at 7.3.1.

7.3.6 Complete the preparation of the sample by carefully uncapping and venting each vessel in a fume hood. Transfer the sample to an acid-cleaned bottle. If the digested sample contains particulates which may clog nebulizers or interfere with injection of the sample into the instrument, the sample may be centrifuged, allowed to settle, or filtered.

7.3.6.1 Centrifugation: Centrifugation at 2,000-3,000 rpm for 10 minutes is usually sufficient to clear the supernatant.

7.3.6.2 Settling: Allow the sample to stand until the supernatant is clear. Allowing a sample to stand overnight will usually accomplish this. If it does not, centrifuge or filter the sample.

7.3.6.3 Filtering: The filtering apparatus must be thoroughly cleaned and prerinsed with dilute (approximately 10% V/V) nitric acid. Filter the sample through qualitative filter paper into a second acid-cleaned container.

7.3.7 Dilute the digest to a known volume ensuring that the samples and standards are matrix matched. The digest is now ready for analysis for elements of interest using the appropriate SW-846 method.

7.4 Calculations: The concentrations determined are to be reported on the basis of the actual weight of the original sample.

8.0 QUALITY CONTROL

8.1 All quality control data must be maintained and available for reference or inspection for a period of three years. This method is restricted to use by, or under supervision of, experienced analysts. Refer to the appropriate section of Chapter One for additional quality control guidance.

8.2 Duplicate samples should be processed on a routine basis. A duplicate sample is a sample brought through the whole sample preparation and analytical process. A duplicate sample should be processed with each analytical batch or every 20 samples, whichever is the greater number. A duplicate sample should be prepared for each matrix type (i.e., soil, sludge, etc.).

8.3 Spiked samples or standard reference materials should be included with each group of samples processed or every 20 samples, whichever is the greater number. A spiked sample should also be included whenever a new sample matrix is being analyzed.

9.0 METHOD PERFORMANCE

9.1 Precision: Precision data for Method 3051, as determined by the statistical examination of interlaboratory test results, is located in Tables 1 and 2.

9.2 Repeatability: If successive results are obtained by the same analyst with the same apparatus under constant operating conditions on identical test material, then the difference between these successive results will not, with 95% probability, exceed the repeatability value. For example, in the case of lead, an average of only 1 case in 20 would exceed

$$0.206\ x$$

in the long run, where x is one result in μg/g (Ref. 6).

9.3 Reproducibility: If two successive measurements are made independently by each of two different analysts working in different laboratories on identical test material, then the difference between the average result for each analyst will not, with 95% probability, exceed the reproducibility value. For example, in the case of lead, an average of only 1 case in 20 would exceed

$$0.303\ x$$

in the long run, where x is the average of two successive measurements in μg/g (Ref. 2).

As can be seen in Table 1, repeatability and reproducibility differ between elements, and usually depend on that element's concentration. Table 2 provides an example of how users of the method can determine expected values for repeatability and reproducibility; nominal values of lead have been used for this model (Ref. 6).

9.4 Bias: In the case of SRM 1085 - Wear Metals in Oil, the bias of this test method is different for each element. An estimate of bias, as shown in Table 3, is:

$$\text{Bias} = \text{Amount found} - \text{Amount expected.}$$

However, the bias estimate inherits both the uncertainty in the measurements made using Method 3051 and the uncertainty on the certificate, so whether the bias is real or only due to measurement error must also be considered. The concentrations found for Al, Cr, and Cu using Method 3051 fall within their certified ranges on SRM 1085, and 95% confidence intervals for Fe and Ni overlap with their respective certified ranges; therefore, the observed biases for these elements are probably due to chance and should be considered insignificant. Biases should not be estimated at all for Ag and Pb because these elements were not certified. Therefore, the only two elements considered in this table for which the bias estimates are significant are Mg and Mo.

10.0 REFERENCES

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2. Kingston, H. M. and L. B. Jassie, "Safety Guidelines for Microwave Systems in the Analytical Laboratory". In Introduction to Microwave Acid Decomposition: Theory and Practice; Kingston, H. M. and Jassie, L. B., eds.; ACS Professional Reference Book Series; American Chemical Society: Washington, DC, 1988.

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7. Kingston, H. M., Walter, P. J., "Comparison of Microwave Versus Conventional Dissolution for Environmental Applications", Spectroscopy, vol. 7 No. 9,20-27,1992.

TABLE 1.
EQUATIONS RELATING REPEATABILITY AND REPRODUCIBILITY TO MEAN CONCENTRATION OF DUPLICATE DETERMINATION WITH 95 PERCENT CONFIDENCE

Element	Repeatability	Reproducibility
Ag	0.195X[a]	0.314X
Al	0.232X	0.444X
B	12.9[b]	22.6[b]
Ba	0.238X	0.421X
Be	0.082[b]	0.082[b]
Ca	0.356X	1.27X
Cd	0.385X	0.571X
Co	0.291X	0.529X
Cr	0.187X	0.195X
Cu	0.212X	0.322X
Fe	0.257X	0.348X
Mg	0.238X	0.399X
Mn	1.96X1/2[c]	4.02X1/2
Mo	0.701X	0.857X
Ni	0.212X	0.390X
Pb	0.206X	0.303X
Sr	0.283X	0.368X
V	1.03X1/2	2.23X1/2
Zn	3.82X1/2	7.69X1/2

[a]Log transformed variable based on one-way analysis of variance.
[b]Repeatability and reproducibility were independent of concentration.
[c]Square root transformed variable based on one-way analysis of variance.

TABLE 2.
REPEATABILITY AND REPRODUCIBILITY FOR LEAD
BY METHOD 3051

Average Value	Repeatability	Reproducibility
50	10.3	15.2
100	20.6	30.3
200	41.2	60.6
300	61.8	90.9
400	82.4	121
500	103	152

All results are in mg/Kg

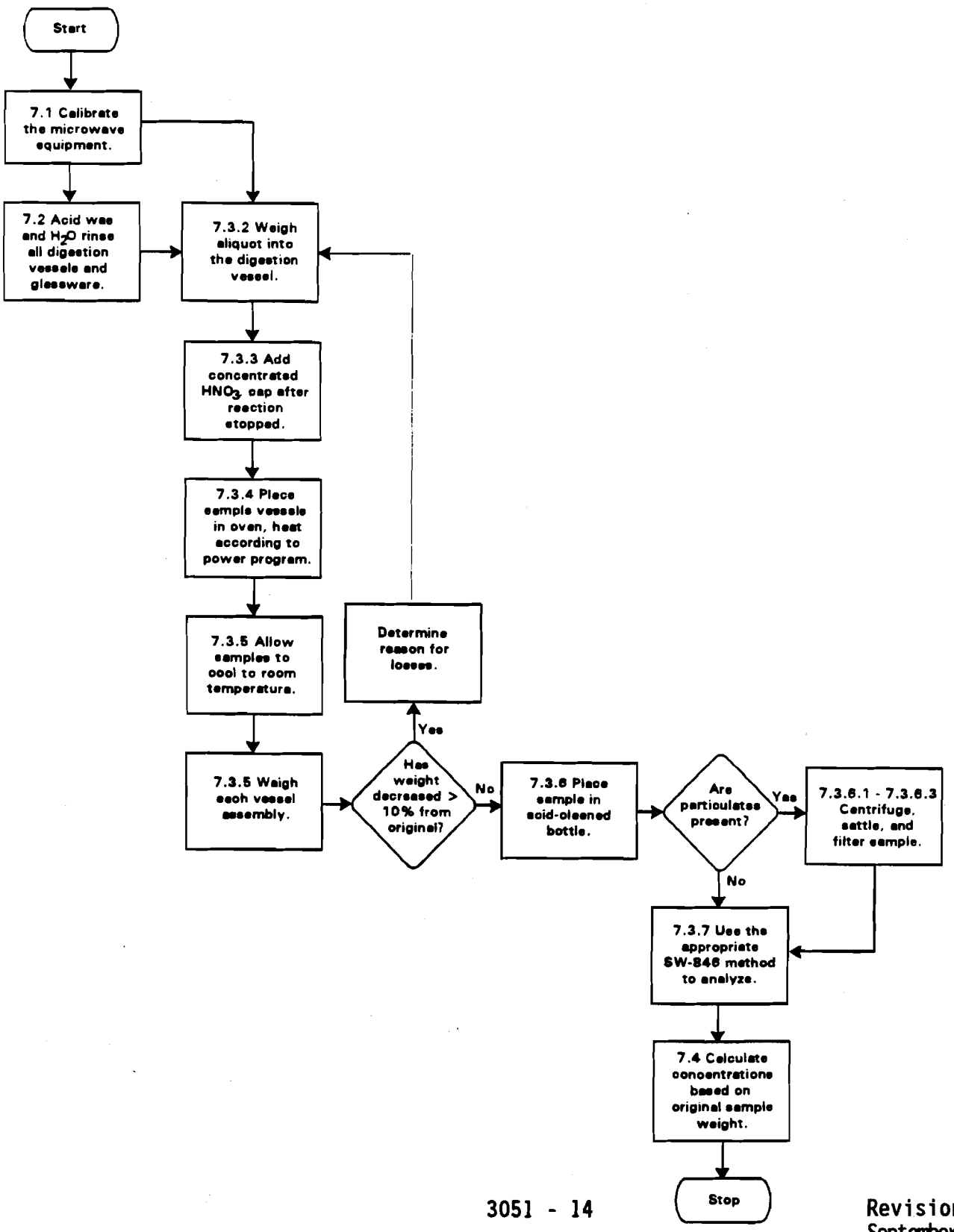
TABLE 3.
RECOVERY AND BIAS DATA FOR SRM 1085 - WEAR METALS IN OIL

Element	Amount Expected (Certified Range)	Amount Found* (95% Conf Interval)	Absolute Bias (μg/g)	Relative Bias (Percent)	Significant (due to more than chance)
Ag	(291)**	234±16	--	--	--
Al	296±4	295±12	-1	0	No
Cr	298±5	293±10	-5	-2	No
Cu	295±10	289±9	-6	-2	No
Fe	300±4	311±14	+11	+4	No
Mg	297±3	270±11	-27	-9	Yes
Mo	292±11	238±11	-54	-18	Yes
Ni	303±7	293±9	-10	-3	No
Pb	(305)**	279±8	--	--	--

All values in mg/Kg

*Results taken from table 4-7, Ref. 2.

**Value not certified, so should not be used in bias detection and estimation.


Start
7.1 Calibrate the microwave equipment.
7.2 Acid wse and H_2O rinse all digestion vessels and glassware.
7.3.2 Weigh aliquot into the digestion vessel.
7.3.3 Add concentrated HNO_3, cap after reaction stopped.
7.3.4 Place sample vessels in oven, heat according to power program.
7.3.5 Allow samples to cool to room temperature.
7.3.5 Weigh each vessel assembly.
Determine reason for losses.
Yes
Has weight decreased > 10% from original?
No
7.3.6 Place sample in acid-cleaned bottle.
Are particulates present?
Yes
7.3.6.1 - 7.3.6.3 Centrifuge, settle, and filter sample.
No
7.3.7 Use the appropriate SW-846 method to analyze.
7.4 Calculate concentrations based on original sample weight.
Stop

3.3 METHODS FOR DETERMINATION OF METALS

This section of the manual contains seven analytical techniques for trace metal determinations: inductively coupled argon plasma atomic emission spectrometry (ICP-AES), inductively coupled plasma mass spectrometry (ICP-MS), direct-aspiration or flame atomic absorption spectrometry (FLAA), graphite-furnace atomic absorption spectrometry (GFAA), hydride-generation atomic absorption spectrometry (HGAA), cold-vapor atomic absorption spectrometry (CVAA), and several procedures for hexavalent chromium analysis. Each of these is briefly discussed below in terms of advantages, disadvantages, and cautions for analysis of wastes.

ICP's primary advantage is that it allows simultaneous or rapid sequential determination of many elements in a short time. The primary disadvantage of ICP is background radiation from other elements and the plasma gases. Although all ICP instruments utilize high-resolution optics and background correction to minimize these interferences, analysis for traces of metals in the presence of a large excess of a single metal is difficult. Examples would be traces of metals in an alloy or traces of metals in a limed (high calcium) waste. ICP and Flame AA have comparable detection limits (within a factor of 4) except that ICP exhibits greater sensitivity for refractories (Al, Ba, etc.). Furnace AA, in general, will exhibit lower detection limits than either ICP or FLAA. Detection limits are drastically improved when ICP-MS is used. In general ICP-MS exhibits greater sensitivity than either GFAA of FLAA for most elements. The greatest disadvantage of ICP-MS is isobaric elemental interferences. These are caused by different elements forming atomic ions with the same nominal mass-to-charge ratio. Mathematical correction for interfering ions can minimize these interferences.

Flame AAS (FLAA) direct aspiration determinations, as opposed to ICP, are normally completed as single element analyses and are relatively free of interelement spectral interferences. Either a nitrous-oxide/acetylene or air/acetylene flame is used as an energy source for dissociating the aspirated sample into the free atomic state making analyte atoms available for absorption of light. In the analysis of some elements the temperature or type of flame used is critical. If the proper flame and analytical conditions are not used, chemical and ionization interferences can occur.

Graphite Furnace AAS (GFAA) replaces the flame with an electrically heated graphite furnace. The furnace allows for gradual heating of the sample aliquot in several stages. Thus, the processes of desolvation, drying, decomposition of organic and inorganic molecules and salts, and formation of atoms which must occur in a flame or ICP in a few milliseconds may be allowed to occur over a much longer time period and at controlled temperatures in the furnace. This allows an experienced analyst to remove unwanted matrix components by using temperature programming and/or matrix modifiers. The major advantage of this technique is that it affords extremely low detection limits. It is the easiest to perform on relatively clean samples. Because this technique is so sensitive, interferences can be a real problem; finding the optimum combination of digestion, heating times and temperatures, and matrix modifiers can be a

challenge for complex matrices.

Hydride AA utilizes a chemical reduction to reduce and separate arsenic or selenium selectively from a sample digestate. The technique therefore has the advantage of being able to isolate these two elements from complex samples which may cause interferences for other analytical procedures. Significant interferences have been reported when any of the following is present: 1) easily reduced metals (Cu, Ag, Hg); 2) high concentrations of transition metals (>200 mg/L); 3) oxidizing agents (oxides of nitrogen) remaining following sample digestion.

Cold-Vapor AA uses a chemical reduction to reduce mercury selectively. The procedure is extremely sensitive but is subject to interferences from some volatile organics, chlorine, and sulfur compounds.

METHOD 6010A

INDUCTIVELY COUPLED PLASMA-ATOMIC EMISSION SPECTROSCOPY

1.0 SCOPE AND APPLICATION

1.1 Inductively coupled plasma-atomic emission spectroscopy (ICP) determines trace elements, including metals, in solution. The method is applicable to all of the elements listed in Table 1. All matrices, including ground water, aqueous samples, TCLP and EP extracts, industrial and organic wastes, soils, sludges, sediments, and other solid wastes, require digestion prior to analysis.

1.2 Elements for which Method 6010 is applicable are listed in Table 1. Detection limits, sensitivity, and optimum ranges of the metals will vary with the matrices and model of spectrometer. The data shown in Table 1 provide estimated detection limits for clean aqueous samples using pneumatic nebulization. Use of this method is restricted to spectroscopists who are knowledgeable in the correction of spectral, chemical, and physical interferences.

2.0 SUMMARY OF METHOD

2.1 Prior to analysis, samples must be solubilized or digested using appropriate Sample Preparation Methods (e.g. Methods 3005-3050). When analyzing for dissolved constituents, acid digestion is not necessary if the samples are filtered and acid preserved prior to analysis.

2.2 Method 6010 describes the simultaneous, or sequential, multielemental determination of elements by ICP. The method measures element-emitted light by optical spectrometry. Samples are nebulized and the resulting aerosol is transported to the plasma torch. Element-specific atomic-line emission spectra are produced by a radio-frequency inductively coupled plasma. The spectra are dispersed by a grating spectrometer, and the intensities of the lines are monitored by photomultiplier tubes. Background correction is required for trace element determination. Background must be measured adjacent to analyte lines on samples during analysis. The position selected for the background-intensity measurement, on either or both sides of the analytical line, will be determined by the complexity of the spectrum adjacent to the analyte line. The position used must be free of spectral interference and reflect the same change in background intensity as occurs at the analyte wavelength measured. Background correction is not required in cases of line broadening where a background correction measurement would actually degrade the analytical result. The possibility of additional interferences named in Section 3.0 should also be recognized and appropriate corrections made; tests for their presence are described in Step 8.5.

TABLE 1.
RECOMMENDED WAVELENGTHS AND ESTIMATED INSTRUMENTAL DETECTION LIMITS

Detection Element	Wavelength[a] (nm)	Estimated Limit[b] (ug/L)
Aluminum	308.215	45
Antimony	206.833	32
Arsenic	193.696	53
Barium	455.403	2
Beryllium	313.042	0.3
Cadmium	226.502	4
Calcium	317.933	10
Chromium	267.716	7
Cobalt	228.616	7
Copper	324.754	6
Iron	259.940	7
Lead	220.353	42
Lithium	670.784	5
Magnesium	279.079	30
Manganese	257.610	2
Molybdenum	202.030	8
Nickel	231.604	15
Phosphorus	213.618	51
Potassium	766.491	See note c
Selenium	196.026	75
Silver	328.068	7
Sodium	588.995	29
Strontium	407.771	0.3
Thallium	190.864	40
Vanadium	292.402	8
Zinc	213.856	2

[a]The wavelengths listed are recommended because of their sensitivity and overall acceptance. Other wavelengths may be substituted if they can provide the needed sensitivity and are treated with the same corrective techniques for spectral interference (see Step 3.1). In time, other elements may be added as more information becomes available and as required.

[b]The estimated instrumental detection limits shown are taken from Reference 1 in Section 10.0 below. They are given as a guide for an instrumental limit. The actual method detection limits are sample dependent and may vary as the sample matrix varies.

[c]Highly dependent on operating conditions and plasma position.

3.0 INTERFERENCES

3.1 Spectral interferences are caused by: (1) overlap of a spectral line from another element at the analytical or background measurement wavelengths; (2) unresolved overlap of molecular band spectra; (3) background contribution from continuum or recombination phenomena; and (4) stray light from the line emission of high-concentration elements. Spectral overlap can be compensated for by computer-correcting the raw data after monitoring and measuring the interfering element. Unresolved overlap requires selection of an alternate wavelength. Background contribution and stray light can usually be compensated for by a background correction adjacent to the analyte line.

Users of all ICP instruments must verify the absence of spectral interference from an element in a sample for which there is no instrument detection channel. Recommended wavelengths are listed in Table 1 and potential spectral interferences for the recommended wavelengths are given in Table 2. The data in Table 2 are intended as rudimentary guides for indicating potential interferences; for this purpose, linear relations between concentration and intensity for the analytes and the interferents can be assumed.

3.1.1 Element-specific interference is expressed as analyte concentration equivalents (i.e. false analyte concentrations) arising from 100 mg/L of the interference element. For example, assume that As is to be determined (at 193.696 nm) in a sample containing approximately 10 mg/L of Al. According to Table 2, 100 mg/L of Al would yield a false signal for As equivalent to approximately 1.3 mg/L. Therefore, the presence of 10 mg/L of Al would result in a false signal for As equivalent to approximately 0.13 mg/L. The user is cautioned that other instruments may exhibit somewhat different levels of interference than those shown in Table 2. The interference effects must be evaluated for each individual instrument since the intensities will vary with operating conditions, power, viewing height, argon flow rate, etc. The user should be aware of the possibility of interferences other than those specified in Table 2 and that analysts should be aware of these interferences when conducting analyses.

3.1.2 The dashes in Table 2 indicate that no measurable interferences were observed even at higher interferent concentrations. Generally, interferences were discernible if they produced peaks, or background shifts, corresponding to 2 to 5% of the peaks generated by the analyte concentrations.

3.1.3 At present, information on the listed silver and potassium wavelengths is not available, but it has been reported that second-order energy from the magnesium 383.231-nm wavelength interferes with the listed potassium line at 766.491 nm.

TABLE 2.

ANALYTE CONCENTRATION EQUIVALENTS ARISING FROM INTERFERENCE AT THE 100-mg/L LEVEL

		Interferent[a,b]									
Analyte	Wavelength (nm)	Al	Ca	Cr	Cu	Fe	Mg	Mn	Ni	Tl	V
Aluminum	308.215	--	--	--	--	--	--	0.21	--	--	1.4
Antimony	206.833	0.47	--	2.9	--	0.08	--	--	--	0.25	0.45
Arsenic	193.696	1.3	--	0.44	--	--	--	--	--	--	1.1
Barium	455.403	--	--	--	--	--	--	--	--	--	--
Beryllium	313.042	--	--	--	--	--	--	--	--	0.04	0.05
Cadmium	226.502	--	--	--	--	0.03	--	--	0.02	--	--
Calcium	317.933	--	--	0.08	--	0.01	0.01	0.04	--	0.03	0.03
Chromium	267.716	--	--	--	--	0.003	--	0.04	--	--	0.04
Cobalt	228.616	--	--	0.03	--	0.005	--	--	0.03	0.15	--
Copper	324.754	--	--	--	--	0.003	--	--	--	0.05	0.02
Iron	259.940	--	--	--	--	--	--	0.12	--	--	--
Lead	220.353	0.17	--	--	--	--	--	--	--	--	--
Magnesium	279.079	--	0.02	0.11	--	0.13	--	0.25	--	0.07	0.12
Manganese	257.610	0.005	--	0.01	--	0.002	0.002	--	--	--	--
Molybdenum	202.030	0.05	--	--	--	0.03	--	--	--	--	--
Nickel	231.604	--	--	--	--	--	--	--	--	--	--
Selenium	196.026	0.23	--	--	--	0.09	--	--	--	--	--
Sodium	588.995	--	--	--	--	--	--	--	--	0.08	--
Thallium	190.864	0.30	--	--	--	--	--	--	--	--	--
Vanadium	292.402	--	--	0.05	--	0.005	--	--	--	0.02	--
Zinc	213.856	--	--	--	0.14	--	--	--	0.29	--	--

[a]Dashes indicate that no interference was observed even when interferents were introduced at the following levels:

Al - 1000 mg/L
Ca - 1000 mg/L
Cr - 200 mg/L
Cu - 200 mg/L
Fe - 1000 mg/L
Mg - 1000 mg/L
Mn - 200 mg/L
Tl - 200 mg/L
V - 200 mg/L

[b]The figures recorded as analyte concentrations are not the actual observed concentrations; to obtain those figures, add the listed concentration to the interferent figure.

3.2 Physical interferences are effects associated with the sample nebulization and transport processes. Changes in viscosity and surface tension can cause significant inaccuracies, especially in samples containing high dissolved solids or high acid concentrations. Differences in solution volatility can also cause inaccuracies when organic solvents are involved. If physical interferences are present, they must be reduced by diluting the sample or by using a peristaltic pump. Another problem that can occur with high dissolved solids is salt buildup at the tip of the nebulizer, which affects aerosol flow rate and causes instrumental drift. The problem can be controlled by wetting the argon prior to nebulization, using a tip washer, or diluting the sample. Changing the nebulizer and removing salt buildup at the tip of the torch sample injector can be used as an additional measure to control salt buildup. Also, it has been reported that better control of the argon flow rate improves instrument performance; this is accomplished with the use of mass flow controllers.

3.3 Chemical interferences include molecular compound formation, ionization effects, and solute vaporization effects. Normally, these effects are not significant with the ICP technique. If observed, they can be minimized by careful selection of operating conditions (incident power, observation position, and so forth), by buffering of the sample, by matrix matching, and by standard addition procedures. Chemical interferences are highly dependent on matrix type and the specific analyte element.

4.0 APPARATUS AND MATERIALS

4.1 Inductively coupled argon plasma emission spectrometer:

4.1.1 Computer-controlled emission spectrometer with background correction.

4.1.2 Radio frequency generator compliant with FCC regulations.

4.1.3 Argon gas supply - Welding grade or better.

4.2 Operating conditions - The analyst should follow the instructions provided by the instrument manufacturer. For operation with organic solvents, use of the auxiliary argon inlet is recommended, as are solvent-resistant tubing, increased plasma (coolant) argon flow, decreased nebulizer flow, and increased RF power to obtain stable operation and precise measurements. Sensitivity, instrumental detection limit, precision, linear dynamic range, and interference effects must be established for each individual analyte line on that particular instrument. All measurements must be within the instrument linear range where spectral interference correction factors are valid. The analyst must (1) verify that the instrument configuration and operating conditions satisfy the analytical requirements and (2) maintain quality control data confirming instrument performance and analytical results.

4.3 Class A volumetric flasks

4.4 Class A volumetric pipets

4.5 Analytical balance - capable of accurate measurement to 4 significant figures.

5.0 REAGENTS

5.1 Reagent grade chemicals shall be used in all tests. Unless otherwise indicated, it is intended that all reagents shall conform to the specifications of the Committee on Analytical Reagents of the American Chemical Society, where such specifications are available. Other grades may be used, provided it is first ascertained that the reagent is of sufficiently high purity to permit its use without lessening the accuracy of the determination. If the purity of a reagent is in question analyze for contamination. If the concentration is less than the MDL then the reagent is acceptable.

5.1.1 Hydrochloric acid (conc), HCl.

5.1.2 Hydrochloric acid (1:1), HCl. Add 500 mL concentrated HCl to 400 mL water and dilute to 1 liter in an appropriate beaker.

5.1.3 Nitric acid (conc), HNO_3.

5.1.4 Nitric acid (1:1), HNO_3. Add 500 mL concentrated HNO_3 to 400 mL water and dilute to 1 liter in an appropriate beaker.

5.2 Reagent Water. All references to water in the method refer to reagent water unless otherwise specified. Reagent water will be interference free. Refer to Chapter One for a definition of reagent water.

5.3 Standard stock solutions may be purchased or prepared from ultra-high purity grade chemicals or metals (99.99 to 99.999% pure). All salts must be dried for 1 hour at 105°C, unless otherwise specified.

CAUTION: Many metal salts are extremely toxic if inhaled or swallowed. Wash hands thoroughly after handling.

Typical stock solution preparation procedures follow. Concentrations are calculated based upon the weight of pure metal added, or with the use of the mole fraction and the weight of the metal salt added.

Metal

$$\text{Concentration (ppm)} = \frac{\text{weight (mg)}}{\text{volume (L)}}$$

Metal salts

$$\text{Concentration (ppm)} = \frac{\text{weight (mg) x mole fraction}}{\text{volume (L)}}$$

5.3.1 Aluminum solution, stock, 1 mL = 1000 ug Al: Dissolve 1.0 g of aluminum metal, weighed accurately to at least four significant figures, in an acid mixture of 4 mL of (1:1) HCl and 1 mL of concentrated HNO_3 in a beaker. Warm gently to effect solution. When solution is complete, transfer quantitatively to a liter flask, add an additional

10 mL of (1:1) HCl and dilute to volume in a 1,000 mL volumetric flask with water.

5.3.2 Antimony solution, stock, 1 mL = 1000 ug Sb: Dissolve 2.70 g $K(SbO)C_4H_4O_6$ (mole fraction Sb = 0.3749), weighed accurately to at least four significant figures, in water, add 10 mL (1:1) HCl, and dilute to volume in a 1,000 mL volumetric flask with water.

5.3.3 Arsenic solution, stock, 1 mL = 1000 ug As: Dissolve 1.30 g of As_2O_3 (mole fraction As = 0.7574), weighed accurately to at least four significant figures, in 100 mL of water containing 0.4 g NaOH. Acidify the solution with 2 mL concentrated HNO_3 and dilute to volume in a 1,000 mL volumetric flask with water

5.3.4 Barium solution, stock, 1 mL = 1000 ug Ba: Dissolve 1.50 g $BaCl_2$ (mole fraction Ba = 0.6595), dried at 250°C for 2 hours, weighed accurately to at least four significant figures, in 10 mL water with 1 mL (1:1) HCl. Add 10.0 mL (1:1) HCl and dilute to volume in a 1,000 mL volumetric flask with water.

5.3.5 Beryllium solution, stock, 1 mL = 1000 ug Be: Do not dry. Dissolve 19.7 g $BeSO_4 \cdot 4H_2O$ (mole fraction Be = 0.0509), weighed accurately to at least four significant figures, in water, add 10.0 mL concentrated HNO_3, and dilute to volume in a 1,000 mL volumetric flask with water.

5.3.6 Cadmium solution, stock, 1 mL = 1000 ug Cd: Dissolve 1.10 g CdO (mole fraction Cd = 0.8754), weighed accurately to at least four significant figures, in a minimum amount of (1:1) HNO_3. Heat to increase rate of dissolution. Add 10.0 mL concentrated HNO_3 and dilute to volume in a 1,000 mL volumetric flask with water.

5.3.7 Calcium solution, stock, 1 mL = 1000 ug Ca: Suspend 2.50 g $CaCO_3$ (mole Ca fraction = 0.4005), dried at 180°C for 1 hour before weighing, weighed accurately to at least four significant figures, in water and dissolve cautiously with a minimum amount of (1:1) HNO_3. Add 10.0 mL concentrated HNO_3 and dilute to volume in a 1,000 mL volumetric flask with water.

5.3.8 Chromium solution, stock, 1 mL = 1000 ug Cr: Dissolve 1.90 g CrO_3 (mole fraction Cr = 0.5200), weighed accurately to at least four significant figures, in water. When solution is complete, acidify with 10 mL concentrated HNO_3 and dilute to volume in a 1,000 mL volumetric flask with water.

5.3.9 Cobalt solution, stock, 1 mL = 1000 ug Co: Dissolve 1.00 g of cobalt metal, weighed accurately to at least four significant figures, in a minimum amount of (1:1) HNO_3. Add 10.0 mL (1:1) HCl and dilute to volume in a 1,000 mL volumetric flask with water.

5.3.10 Copper solution, stock, 1 mL = 1000 ug Cu: Dissolve 1.30 g CuO (mole fraction Cu = 0.7989), weighed accurately to at least four significant figures), in a minimum amount of (1:1) HNO_3. Add 10.0 mL

concentrated HNO_3 and dilute to volume in a 1,000 mL volumetric flask with water.

5.3.11 Iron solution, stock, 1 mL = 1000 ug Fe: Dissolve 1.40 g Fe_2O_3 (mole fraction Fe = 0.6994), weighed accurately to at least four significant figures, in a warm mixture of 20 mL (1:1) HCl and 2 mL of concentrated HNO_3. Cool, add an additional 5.0 mL of concentrated HNO_3, and dilute to volume in a 1,000 mL volumetric flask with water.

5.3.12 Lead solution, stock, 1 mL = 1000 ug Pb: Dissolve 1.60 g $Pb(NO_3)_2$ (mole fraction Pb = 0.6256), weighed accurately to at least four significant figures, in a minimum amount of (1:1) HNO_3. Add 10 mL (1:1) HNO_3 and dilute to volume in a 1,000 mL volumetric flask with water.

5.3.13 Lithium solution, stock, 1 mL = 1000 ug Li: Dissolve 5.324 g lithium carbonate (mole fraction Li = 0.1878), weighed accurately to at least four significant figures, in a minimum amount of (1:1) HCl and dilute to volume in a 1,000 mL volumetric flask with water.

5.3.14 Magnesium solution, stock, 1 mL = 1000 ug Mg: Dissolve 1.70 g MgO (mole fraction Mg = 0.6030), weighed accurately to at least four significant figures, in a minimum amount of (1:1) HNO_3. Add 10.0 mL (1:1) concentrated HNO_3 and dilute to volume in a 1,000 mL volumetric flask with water.

5.3.15 Manganese solution, stock, 1 mL = 1000 ug Mn: Dissolve 1.00 g of manganese metal, weighed accurately to at least four significant figures, in acid mixture (10 mL concentrated HCl and 1 mL concentrated HNO_3) and dilute to volume in a 1,000 mL volumetric flask with water.

5.3.16 Molybdenum solution, stock, 1 mL = 1000 ug Mo: Dissolve 2.00 g $(NH_4)_6Mo_7O_{24}.4H_2O$ (mole fraction Mo = 0.5772), weighed accurately to at least four significant figures, in water and dilute to volume in a 1,000 mL volumetric flask with water.

5.3.17 Nickel solution, stock, 1 mL = 1000 ug Ni: Dissolve 1.00 g of nickel metal, weighed accurately to at least four significant figures, in 10.0 mL hot concentrated HNO_3, cool, and dilute to volume in a 1,000 mL volumetric flask with water.

5.3.18 Phosphate solution, stock, 1 mL = 1000 ug P: Dissolve 4.393 g anhydrous KH_2PO_4 (mole fraction P = 0.2276), weighed accurately to at least four significant figures, in water. Dilute to volume in a 1,000 mL volumetric flask with water.

5.3.19 Potassium solution, stock, 1 mL = 1000 ug K: Dissolve 1.90 g KCl (mole fraction K = 0.5244) dried at 110°C, weighed accurately to at least four significant figures, in water, and dilute to volume in a 1,000 mL volumetric flask with water.

5.3.20 Selenium solution, stock, 1 mL = 1000 ug Se: Do not dry. Dissolve 1.70 g H_2SeO_3 (mole fraction Se = 0.6123), weighed accurately to

at least four significant figures, in water and dilute to volume in a 1,000 mL volumetric flask with water.

5.3.21 Silver solution, stock, 1 mL = 1000 ug Ag: Dissolve 1.60 g $AgNO_3$ (mole fraction Ag = 0.6350), weighed accurately to at least four significant figures, in water and 10 mL concentrated HNO_3. Dilute to volume in a 1,000 mL volumetric flask with water.

5.3.22 Sodium solution, stock, 1 mL = 1000 ug Na: Dissolve 2.50 g NaCl (mole fraction Na = 0.3934), weighed accurately to at least four significant figures, in water. Add 10.0 mL concentrated HNO_3 and dilute to volume in a 1,000 mL volumetric flask with water.

5.3.23 Strontium solution, stock, 1 mL = 1000 ug Sr: Dissolve 2.415 g of strontium nitrate ($Sr(NO_3)_2$) (mole fraction 0.4140), weighed accurately to at least four significant figures, in a 1-liter flask containing 10 mL of concentrated HCl and 700 mL of water. Dilute to volume in a 1,000 mL volumetric flask with water.

5.3.24 Thallium solution, stock, 1 mL = 1000 ug Tl: Dissolve 1.30 g $TlNO_3$ (mole fraction Tl = 0.7672), weighed accurately to at least four significant figures, in water. Add 10.0 mL concentrated HNO_3 and dilute to volume in a 1,000 mL volumetric flask with water.

5.3.25 Vanadium solution, stock, 1 mL = 1000 ug V: Dissolve 2.30 g NH_4O_3 (mole fraction V = 0.4356), weighed accurately to at least four significant figures, in a minimum amount of concentrated HNO_3. Heat to increase rate of dissolution. Add 10.0 mL concentrated HNO_3 and dilute to volume in a 1,000 mL volumetric flask with water.

5.3.26 Zinc solution, stock, 1 mL = 1000 ug Zn: Dissolve 1.20 g ZnO (mole fraction Zn = 0.8034), weighed accurately to at least four significant figures, in a minimum amount of dilute HNO_3. Add 10.0 mL concentrated HNO_3 and dilute to volume in a 1,000 mL volumetric flask with water.

5.4 Mixed calibration standard solutions - Prepare mixed calibration standard solutions by combining appropriate volumes of the stock solutions in volumetric flasks (see Table 3). Matrix match with the appropriate acids and dilute to 100 mL with water. Prior to preparing the mixed standards, each stock solution should be analyzed separately to determine possible spectral interference or the presence of impurities. Care should be taken when preparing the mixed standards to ensure that the elements are compatible and stable together. Transfer the mixed standard solutions to FEP fluorocarbon or previously unused polyethylene or polypropylene bottles for storage. Fresh mixed standards should be prepared, as needed, with the realization that concentration can change on aging. Calibration standards must be initially verified using a quality control sample (see Step 5.8) and monitored weekly for stability. Some typical calibration standard combinations are listed in Table 3. All mixtures should then be scanned using a sequential spectrometer to verify the absence of interelement spectral interference in the recommended mixed standard solutions.

NOTE: If the addition of silver to the recommended acid combination results in an initial precipitation, add 15 mL of water and warm the flask until the solution clears. Cool and dilute to 100 mL with water. For this acid combination, the silver concentration should be limited to 2 mg/L. Silver under these conditions is stable in a tap-water matrix for 30 days. Higher concentrations of silver require additional HCl.

TABLE 3.
MIXED STANDARD SOLUTIONS

Solution	Elements
I	Be, Cd, Mn, Pb, Se and Zn
II	Ba, Co, Cu, Fe, and V
III	As, Mo
IV	Al, Ca, Cr, K, Na, Ni,Li,& Sr
V	Ag (see Note to Step 5.4), Mg, Sb, and Tl
VI	P

5.5 Two types of blanks are required for the analysis. The calibration blank is used in establishing the analytical curve, and the reagent blank is used to correct for possible contamination resulting from varying amounts of the acids used in the sample processing.

5.5.1 The calibration blank is prepared by acidifying reagent water to the same concentrations of the acids found in the standards and samples. Prepare a sufficient quantity to flush the system between standards and samples.

5.5.2 The method blank must contain all the reagents and in the same volumes as used in the processing of the samples. The method blank must be carried through the complete procedure and contain the same acid concentration in the final solution as the sample solution used for analysis.

5.6 The instrument check standard is prepared by the analyst by combining compatible elements at concentrations equivalent to the midpoint of their respective calibration curves (see Step 8.6.1.1 for use). The instrument check standard should be prepared from a source independent from that used in the calibration standards.

5.7 The interference check solution is prepared to contain known concentrations of interfering elements that will provide an adequate test of the correction factors. Spike the sample with the elements of interest at approximate

5.7 The interference check solution is prepared to contain known concentrations of interfering elements that will provide an adequate test of the correction factors. Spike the sample with the elements of interest at approximate concentrations of 10 times the instrumental detection limits. In the absence of measurable analyte, overcorrection could go undetected because a negative value could be reported as zero. If the particular instrument will display overcorrection as a negative number, this spiking procedure will not be necessary.

5.8 The quality control sample should be prepared in the same acid matrix as the calibration standards at 10 times the instrumental detection limits and in accordance with the instructions provided by the supplier.

6.0 SAMPLE COLLECTION, PRESERVATION, AND HANDLING

6.1 See the material in Chapter Three, Metallic Analytes, Steps 3.1 through 3.3.

7.0 PROCEDURE

7.1 Preliminary treatment of most matrices is necessary because of the complexity and variability of sample matrices. Water samples which have been prefiltered and acidified will not need acid digestion as long as the samples and standards are matrix matched. Solubilization and digestion procedures are presented in Sample Preparation Methods (Methods 3005A-3050A).

7.2 Set up the instrument with proper operating parameters established in Step 4.2. The instrument must be allowed to become thermally stable before beginning (usually requiring at least 30 minutes of operation prior to calibration).

7.3 Profile and calibrate the instrument according to the instrument manufacturer's recommended procedures, using the typical mixed calibration standard solutions described in Step 5.4. Flush the system with the calibration blank (Step 5.5.1) between each standard or as the manufacturer recommends. (Use the average intensity of multiple exposures for both standardization and sample analysis to reduce random error.) The calibration curve should consist of a blank and three standards.

7.4 Before beginning the sample run, reanalyze the highest mixed calibration standard as if it were a sample. Concentration values obtained should not deviate from the actual values by more than 5% (or the established control limits, whichever is lower). If they do, follow the recommendations of the instrument manufacturer to correct for this condition.

7.5 Flush the system with the calibration blank solution for at least 1 minute (Step 5.5.1) before the analysis of each sample (see Note to Step 7.3). Analyze the instrument check standard (Step 5.6) and the calibration blank (Step 5.5.1) after each 10 samples.

8.0 QUALITY CONTROL

8.1 All quality control data should be maintained and available for easy reference or inspection. Refer to Chapter One for additional quality control procedures.

8.2 Dilute and reanalyze samples that are more concentrated than the linear calibration limit or use an alternate, less sensitive line for which quality control data is already established.

8.3 Employ a minimum of one method blank per sample batch to determine if contamination or any memory effects are occurring. A method blank is a volume of reagent water acidified with the same amounts of acids as were the standards and samples.

8.4 Analyze one replicate sample for every twenty samples or per analytical batch, whichever is more frequent. A replicate sample is a sample brought through the whole sample preparation and analytical process in duplicate. Refer to Chapter One for a more detailed description of an analytical batch.

8.5 It is recommended that whenever a new or unusual sample matrix is encountered, a series of tests be performed prior to reporting concentration data for analyte elements. These tests, as outlined in Steps 8.5.1 and 8.5.2, will ensure the analyst that neither positive nor negative interferences are operating on any of the analyte elements to distort the accuracy of the reported values.

8.5.1 Serial dilution: If the analyte concentration is sufficiently high (minimally, a factor of 10 above the instrumental detection limit after dilution), an analysis of a 1:4 dilution should agree within $\pm$ 10% of the original determination. If not, a chemical or physical interference effect should be suspected.

8.5.2 Post digestion spike addition: An analyte spike added to a portion of a prepared sample, or its dilution, should be recovered to within 75% to 125% of the known value. The spike addition should produce a minimum level of 10 times and a maximum of 100 times the instrumental detection limit. If the spike is not recovered within the specified limits, a matrix effect should be suspected.

CAUTION: If spectral overlap is suspected, use of computerized compensation, an alternate wavelength, or comparison with an alternate method is recommended.

8.6 Check the instrument standardization by analyzing appropriate check standards as follows.

8.6.1 Verify calibration every 10 samples and at the end of the analytical run, using a calibration blank (Step 5.5.1) and a check standard (Step 5.6).

8.6.1.1 The results of the check standard are to agree within 10% of the expected value; if not, terminate the analysis, correct the problem, and reanalyze the previous ten samples.

8.6.1.2 The results of the calibration blank are to agree within three standard deviations of the mean blank value. If not, repeat the analysis two more times and average the results. If the average is not within three standard deviations of the background mean, terminate the analysis, correct the problem, recalibrate, and reanalyze the previous 10 samples.

8.6.2 Verify the interelement and background correction factors at the beginning and end of an analytical run or twice during every 8-hour work shift, whichever is more frequent. Do this by analyzing the interference check solution (Step 5.7). Results should be within ± 20% of the true value obtained in Step 8.6.1.1.

8.6.3 Spiked replicate samples are to be analyzed at a frequency of 5% or per analytical batch, whichever is more frequent.

8.6.3.1 The relative percent difference between replicate determinations is to be calculated as follows:

$$RPD = \frac{D_1 - D_2}{(D_1 + D_2)/2} \times 100$$

where:

RPD = relative percent difference.
D_1 = first sample value.
D_2 = second sample value (replicate).

(A control limit of ± 20% RPD shall be used for sample values greater than ten times the instrument detection limit.)

8.6.3.2 The spiked replicate sample recovery is to be within ± 20% of the actual value.

9.0 METHOD PERFORMANCE

9.1 In an EPA round-robin Phase 1 study, seven laboratories applied the ICP technique to acid-distilled water matrices that had been spiked with various metal concentrates. Table 4 lists the true values, the mean reported values, and the mean percent relative standard deviations.

9.2 In a single laboratory evaluation, seven wastes were analyzed for 22 elements by this method. The mean percent relative standard deviation from triplicate analyses for all elements and wastes was 9 ± 2%. The mean percent recovery of spiked elements for all wastes was 93 ± 6%. Spike levels ranged from 100 ug/L to 100 mg/L. The wastes included sludges and industrial wastewaters.

10.0 REFERENCES

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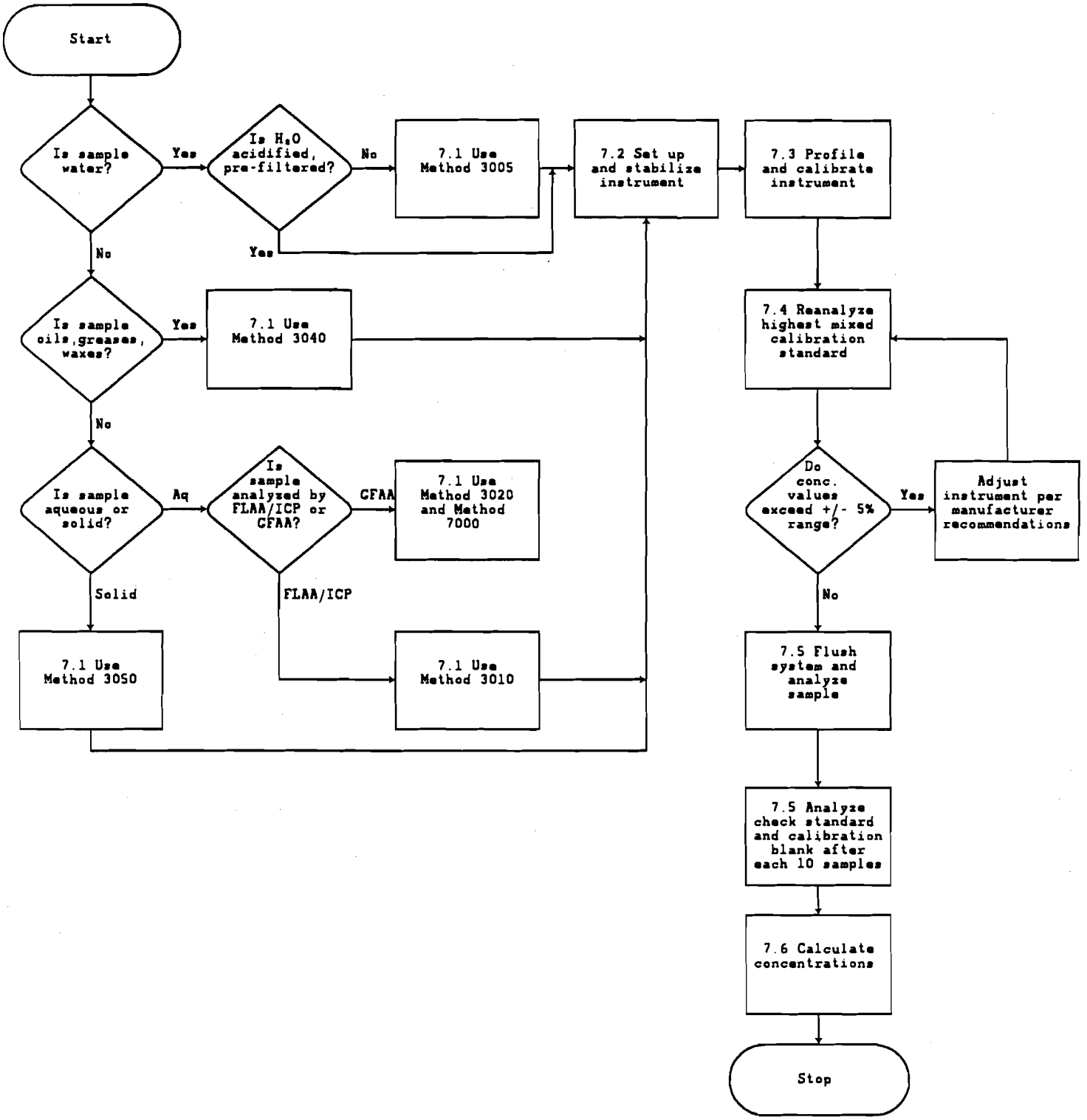
TABLE 4.
ICP PRECISION AND ACCURACY DATA[a]

	Sample No. 1			Sample No. 2			Sample No. 3		
Element	True Value (ug/L)	Mean Reported Value (ug/L)	Mean SD[b] (%)	True Value (ug/L)	Mean Reported Value (ug/L)	Mean SD[b] (%)	True Value (ug/L)	Mean Reported Value (ug/L)	Mean SD[b] (%)
Be	750	733	6.2	20	20	9.8	180	176	5.2
Mn	350	345	2.7	15	15	6.7	100	99	3.3
V	750	749	1.8	70	69	2.9	170	169	1.1
As	200	208	7.5	22	19	23	60	63	17
Cr	150	149	3.8	10	10	18	50	50	3.3
Cu	250	235	5.1	11	11	40	70	67	7.9
Fe	600	594	3.0	20	19	15	180	178	6.0
Al	700	696	5.6	60	62	33	160	161	13
Cd	50	48	12	2.5	2.9	16	14	13	16
Co	700	512	10	20	20	4.1	120	108	21
Ni	250	245	5.8	30	28	11	60	55	14
Pb	250	236	16	24	30	32	80	80	14
Zn	200	201	5.6	16	19	45	80	82	9.4
Se[c]	40	32	21.9	6	8.5	42	10	8.5	8.3

[a]Not all elements were analyzed by all laboratories.

[b]SD = standard deviation.

[c]Results for Se are from two laboratories.


Start
Is sample water?
Yes
Is H_2O acidified, pre-filtered?
No
7.1 Use Method 3005
Yes
7.2 Set up and stabilize instrument
7.3 Profile and calibrate instrument
No
Is sample oils,greases, waxes?
Yes
7.1 Use Method 3040
7.4 Reanalyze highest mixed calibration standard
No
Is sample aqueous or solid?
Aq
Is sample analyzed by FLAA/ICP or CFAA?
CFAA
7.1 Use Method 3020 and Method 7000
Do conc. values exceed +/- 5% range?
Yes
Adjust instrument per manufacturer recommendations
Solid
FLAA/ICP
No
7.1 Use Method 3050
7.1 Use Method 3010
7.5 Flush system and analyze sample
7.5 Analyze check standard and calibration blank after each 10 samples
7.6 Calculate concentrations
Stop

METHOD 6020

INDUCTIVELY COUPLED PLASMA - MASS SPECTROMETRY

1.0 SCOPE AND APPLICATION

1.1 Inductively coupled plasma-mass spectrometry (ICP-MS) is applicable to the determination of sub-μg/L concentrations of a large number of elements in water samples and in waste extracts or digests [1,2]. When dissolved constituents are required, samples must be filtered and acid-preserved prior to analysis. No digestion is required prior to analysis for dissolved elements in water samples. Acid digestion prior to filtration and analysis is required for groundwater, aqueous samples, industrial wastes, soils, sludges, sediments, and other solid wastes for which total (acid-leachable) elements are required.

1.2 ICP-MS has been applied to the determination of over 60 elements in various matrices. Analytes for which EPA has demonstrated the acceptability of Method 6020 in a multi-laboratory study on solid wastes are listed in Table 1. Acceptability of the method for an element was based upon the multi-laboratory performance compared with that of either furnace atomic absorption spectroscopy or inductively coupled plasma-atomic emission spectroscopy. It should be noted that the multi-laboratory study was conducted in 1986. Multi-laboratory performance data for the listed elements (and others) are provided in Section 9. Instrument detection limits, sensitivities, and linear ranges will vary with the matrices, instrumentation, and operating conditions. In relatively simple matrices, detection limits will generally be below 0.02 μg/L.

1.3 If Method 6020 is used to determine any analyte not listed in Table 1, it is the responsibility of the analyst to demonstrate the accuracy and precision of the Method in the waste to be analyzed. The analyst is always required to monitor potential sources of interferences and take appropriate action to ensure data of known quality (see Section 8.4).

1.4 Use of this method is restricted to spectroscopists who are knowledgeable in the recognition and in the correction of spectral, chemical, and physical interferences in ICP-MS.

1.5 An appropriate internal standard is required for each analyte determined by ICP-MS. Recommended internal standards are ^{6}Li, ^{45}Sc, ^{89}Y, ^{103}Rh, ^{115}In, ^{159}Tb, ^{165}Ho, and ^{209}Bi. The lithium internal standard should have an enriched abundance of ^{6}Li, so that interference from lithium native to the sample is minimized. Other elements may need to be used as internal standards when samples contain significant amounts of the recommended internal standards.

2.0 SUMMARY OF METHOD

2.1 Prior to analysis, samples which require total ("acid-leachable") values must be digested using appropriate sample preparation methods (such as Methods 3005 - 3051).

2.2 Method 6020 describes the multi-elemental determination of analytes by ICP-MS. The method measures ions produced by a radio-frequency inductively coupled plasma. Analyte species originating in a liquid are nebulized and the resulting aerosol transported by argon gas into the plasma torch. The ions produced are entrained in the plasma gas and introduced, by means of an interface, into a mass spectrometer. The ions produced in the plasma are sorted according to their mass-to-charge ratios and quantified with a channel electron multiplier. Interferences must be assessed and valid corrections applied or the data flagged to indicate problems. Interference correction must include compensation for background ions contributed by the plasma gas, reagents, and constituents of the sample matrix.

3.0 INTERFERENCES

3.1 Isobaric elemental interferences in ICP-MS are caused by isotopes of different elements forming atomic ions with the same nominal mass-to-charge ratio (m/z). A data system must be used to correct for these interferences. This involves determining the signal for another isotope of the interfering element and subtracting the appropriate signal from the analyte isotope signal. Since commercial ICP-MS instruments nominally provide unit resolution at 10% of the peak height, very high ion currents at adjacent masses can also contribute to ion signals at the mass of interest. Although this type of interference is uncommon, it is not easily corrected, and samples exhibiting a significant problem of this type could require resolution improvement, matrix separation, or analysis using another verified and documented isoptope, or use of another method.

3.2 Isobaric molecular and doubly-charged ion interferences in ICP-MS are caused by ions consisting of more than one atom or charge, respectively. Most isobaric interferences that could affect ICP-MS determinations have been identified in the literature [3,4]. Examples include $ArCl^+$ ions on the ^{75}As signal and MoO^+ ions on the cadmium isotopes. While the approach used to correct for molecular isobaric interferences is demonstrated below using the natural isotope abundances from the literature [5], the most precise coefficients for an instrument can be determined from the ratio of the net isotope signals observed for a standard solution at a concentration providing suitable (<1 percent) counting statistics. Because the ^{35}Cl natural abundance of 75.77 percent is 3.13 times the ^{37}Cl abundance of 24.23 percent, the chloride correction for arsenic can be calculated (approximately) as follows (where the $^{38}Ar^{37}Cl^+$ contribution at m/z 75 is a negligible 0.06 percent of the $^{40}Ar^{35}Cl^+$ signal):

> corrected arsenic signal (using natural isotopes abundances for coefficient approximations) =
>
> (m/z 75 signal) - (3.13) (m/z 77 signal) + (2.73) (m/z 82 signal), (where the final term adjusts for any selenium contribution at 77 m/z),
>
> NOTE: Arsenic values can be biased high by this type of equation when the net signal at m/z 82 is caused by ions other than $^{82}Se^+$, (e.g., $^{81}BrH^+$ from bromine wastes [6]).

Similarly,

corrected cadmium signal (using natural isotopes abundances for coefficient approximations) =

(m/z 114 signal) - (0.027)(m/z 118 signal) - (1.63)(m/z 108 signal), (where last 2 terms adjust for any tin or MoO^+ contributions at m/z 114).

NOTE: Cadmium values will be biased low by this type of equation when $^{92}ZrO^+$ ions contribute at m/z 108, but use of m/z 111 for Cd is even subject to direct ($^{94}ZrOH^+$) and indirect ($^{90}ZrO^+$) additive interferences when Zr is present.

NOTE: As for the arsenic equation above, the coefficients in the Cd equation are **ONLY** illustrative. The most appropriate coefficients for an instrument can be determined from the ratio of the net isotope signals observed for a standard solution at a concentration providing suitable (<1 percent) counting precision.

The accuracy of these types of equations is based upon the constancy of the OBSERVED isotopic ratios for the interfering species. Corrections that presume a constant fraction of a molecular ion relative to the "parent" ion have not been found [7] to be reliable, e.g., oxide levels can vary. If a correction for an oxide ion is based upon the ratio of parent-to-oxide ion intensities, the correction must be adjusted for the degree of oxide formation by the use of an appropriate oxide internal standard previously demonstrated to form a similar level of oxide as the interferant. This type of correction has been reported [7] for oxide-ion corrections using ThO^+/Th^+ for the determination of rare earth elements. The use of aerosol desolvation and/or mixed plasmas have been shown to greatly reduce molecular interferences [8]. These techniques can be used provided that method detection limits, accuracy, and precision requirements for analysis of the samples can be met.

3.3 Physical interferences are associated with the sample nebulization and transport processes as well as with ion-transmission efficiencies. Nebulization and transport processes can be affected if a matrix component causes a change in surface tension or viscosity. Changes in matrix composition can cause significant signal suppression or enhancement [9]. Dissolved solids can deposit on the nebulizer tip of a pneumatic nebulizer and on the interface skimmers (reducing the orifice size and the instrument performance). Total solid levels below 0.2% (2,000 mg/L) have been currently recommended [10] to minimize solid deposition. An internal standard can be used to correct for physical interferences, if it is carefully matched to the analyte so that the two elements are similarly affected by matrix changes [11]. When the intensity level of an internal standard is less than 30 percent or greater than 120 percent of the intensity of the first standard used during calibration, the sample must be reanalyzed after a fivefold (1+4) or greater dilution has been performed.

3.4 Memory interferences can occur when there are large concentration differences between samples or standards which are analyzed sequentially. Sample

deposition on the sampler and skimmer cones, spray chamber design, and the type of nebulizer affect the extent of the memory interferences which are observed. The rinse period between samples must be long enough to eliminate significant memory interference.

4.0 APPARATUS AND MATERIALS

4.1 Inductively coupled plasma-mass spectrometer:

4.1.1 A system capable of providing resolution, better than or equal to amu at 10% peak height is required. The system must have a mass range from at least 6 to 240 amu and a data system that allows corrections for isobaric interferences and the application of the internal standard technique. Use of a mass-flow controller for the nebulizer argon and a peristaltic pump for the sample solution are recommended.

4.1.2 Argon gas supply: high-purity grade (99.99%).

5.0 REAGENTS

5.1 Acids used in the preparation of standards and for sample processing must be of high purity. Redistilled acids are recommended because of the high sensitivity of ICP-MS. Nitric acid at less than 2 per cent (v/v) is required for ICP-MS to minimize damage to the interface and to minimize isobaric molecular-ion interferences with the analytes. Many more molecular-ion interferences are observed on the analytes when hydrochloric and sulfuric acids are used [3,4]. Concentrations of antimony and silver between 50-500 μg/L require 1% (v/v) HCl for stability; for concentrations above 500 μg/L Ag, additional HCl will be needed.

5.2 Reagent water: All references to water in the method refer to reagent water unless otherwise specified. Refer to Chapter One for a definition of reagent water.

5.3 Standard stock solutions may be purchased or prepared from ultra-high purity grade chemicals or metals (99.99 or greater purity). See Method 6010A, Section 5.3, for instructions on preparing standard solutions from solids.

5.3.1 Bismuth internal standard solution, stock, 1 mL = 100 μg Bi: Dissolve 0.1115 g Bi_2O_3 in a minimum amount of dilute HNO_3. Add 10 mL conc. HNO_3 and dilute to 1,000 mL with reagent water.

5.3.2 Holmium internal standard solution, stock, 1 mL = 100 μg Ho: Dissolve 0.1757 g $Ho_2(CO_3)_2 \cdot 5H_2O$ in 10 mL reagent water and 10 mL HNO_3. After dissolution is complete, warm the solution to degas. Add 10 mL conc. HNO_3 and dilute to 1,000 mL with reagent water.

5.3.3 Indium internal standard solution, stock, 1 mL = 100 μg In: Dissolve 0.1000 g indium metal in 10 mL conc. HNO_3. Dilute to 1,000 mL with reagent water.

5.3.4 Lithium internal standard solution, stock, 1 mL = 100 µg ^{6}Li: Dissolve 0.6312 g 95-atom-% ^{6}Li, Li_2CO_3 in 10 mL of reagent water and 10 mL HNO_3. After dissolution is complete, warm the solution to degas. Add 10 mL conc. HNO_3 and dilute to 1,000 mL with reagent water.

5.3.5 Rhodium internal standard solution, stock, 1 mL = 100 µg Rh: Dissolve 0.3593 g ammonium hexachlororhodate (III) $(NH_4)_3RhCl_6$ in 10 mL reagent water. Add 100 mL conc. HCl and dilute to 1,000 mL with reagent water.

5.3.6 Scandium internal standard solution, stock, 1 mL = 100 µg Sc: Dissolve 0.15343 g Sc_2O_3 in 10 mL (1+1) hot HNO_3. Add 5 mL conc. HNO_3 and dilute to 1,000 mL with reagent water.

5.3.7 Terbium internal standard solution, stock, 1 mL = 100 µg Tb: Dissolve 0.1828 g $Tb_2(CO_3)_3 \cdot 5H_2O$ in 10 mL (1+1) HNO_3. After dissolution is complete, warm the solution to degas. Add 5 mL conc. HNO_3 and dilute to 1,000 mL with reagent water.

5.3.8 Yttrium internal standard solution, stock, 1 mL = 100 µg Y: Dissolve 0.2316 g $Y_2(CO_3)_3.3H_2O$ in 10 mL (1+1) HNO_3. Add 5 mL conc. HNO_3 and dilute to 1,000 mL with reagent water.

5.3.9 Titanium solution, stock, 1 mL = 100 µg Ti: Dissolve 0.4133 g $(NH_4)_2TiF_6$ in reagent water. Add 2 drops conc. HF and dilute to 1,000 mL with reagent water.

5.3.10 Molybdenum solution, stock, 1 mL = 100 µg Mo: Dissolve 0.2043 g $(NH_4)_2MoO_4$ in reagent water. Dilute to 1,000 mL with reagent water.

5.4 Mixed calibration standard solutions are prepared by diluting the stock-standard solutions to levels in the linear range for the instrument in a solvent consisting of 1 percent (v/v) HNO_3 in reagent water. The calibration standard solutions must contain a suitable concentration of an appropriate internal standard for each analyte. Internal standards may be added on-line at the time of analysis using a second channel of the peristaltic pump and an appropriate mixing manifold.) Generally, an internal standard should be no more than 50 amu removed from the analyte. Recommended internal standards include ^{6}Li, ^{45}Sc, ^{89}Y, ^{103}Rh, ^{115}In, ^{159}Tb, ^{169}Ho, and ^{209}Bi. Prior to preparing the mixed standards, each stock solution must be analyzed separately to determine possible spectral interferences or the presence of impurities. Care must be taken when preparing the mixed standards that the elements are compatible and stable. Transfer the mixed standard solutions to freshly acid-cleaned FEP fluorocarbon bottles for storage. Fresh mixed standards must be prepared as needed with the realization that concentrations can change on aging. Calibration standards must be initially verified using a quality control standard (see Section 5.7) and monitored weekly for stability.

5.5 Blanks: Three types of blanks are required for the analysis. The calibration blank is used in establishing the calibration curve. The preparation blank is used to monitor for possible contamination resulting from the sample preparation procedure. The rinse blank is used to flush the system between all samples and standards.

5.5.1 The calibration blank consists of the same concentration(s) of the same acid(s) used to prepare the final dilution of the calibrating solutions of the analytes [often 1 percent HNO_3 (v/v) in reagent water] along with the selected concentrations of internal standards such that there is an appropriate internal standard element for each of the analytes. Use of HCl for antimony and silver is cited in Section 5.1

5.5.2 The preparation (or reagent) blank must be carried through the complete preparation procedure and contain the same volumes of reagents as the sample solutions.

5.5.3 The rinse blank consists of 1 to 2 percent HNO_3 (v/v) in reagent water. Prepare a sufficient quantity to flush the system between standards and samples.

NOTE: The ICS solutions in Table 2 are intended to evaluate corrections for known interferences on only the analytes in Table 1. If Method 6020 is used to determine an element not listed in Table 1, it is the responsibility of the analyst to modify the ICS solutions, or prepare an alternative ICS solution, to allow adequate verification of correction of interferences on the unlisted element (see section 8.4).

5.6 The interference check solution (ICS) is prepared to contain known concentrations of interfering elements that will demonstrate the magnitude of interferences and provide an adequate test of any corrections. Chloride in the ICS provides a means to evaluate software corrections for chloride-related interferences such as $^{35}Cl^{16}O^+$ on $^{51}V^+$ and $^{40}Ar^{35}Cl^+$ on $^{75}As^+$. Iron is used to demonstrate adequate resolution of the spectrometer for the determination of manganese. Molybdenum serves to indicate oxide effects on cadmium isotopes. The other components are present to evaluate the ability of the measurement system to correct for various molecular-ion isobaric interferences. The ICS is used to verify that the interference levels are corrected by the data system within quality control limits.

5.6.1 These solutions must be prepared from ultra-pure reagents. They can be obtained commercially or prepared by the following procedure.

5.6.1.1 Mixed ICS solution I may be prepared by adding 13.903 g $Al(NO_3)_3 \cdot 9H_2O$, 2.498 g $CaCO_3$ (dried at 180 C for 1 h before weighing), 1.000 g Fe, 1.658 g MgO, 2.305 g Na_2CO_3, and 1.767 g K_2CO_3 to 25 mL of reagent water. Slowly add 40 mL of (1+1) HNO_3. After dissolution is complete, warm the solution to degas. Cool and dilute to 1,000 mL with reagent water.

5.6.1.2 Mixed ICS solution II may be prepared by slowly adding 7.444 g 85 % H_3PO_4, 6.373 g 96% H_2SO_4, 40.024 g 37% HCl, and 10.664 g citric acid $C_6O_7H_8$ to 100 mL of reagent water. Dilute to 1,000 mL with reagent water.

5.6.1.3 Mixed ICS solution III may be prepared by adding 1.00 mL each of 100-μg/mL arsenic, cadmium, chromium, cobalt, copper, manganese, nickel, silver, and zinc stock solutions to about 50 mL reagent water. Add 2.0 mL concentrated HNO_3, and dilute to 100.0 mL with reagent water.

5.6.1.4 Working ICS Solutions

5.6.1.4.1 ICS-A may be prepared by adding 10.0 mL of mixed ICS solution I (5.7.1.1), 2.0 mL each of 100-μg/mL titanium stock solution (5.3.9) and molybdenum stock solution (5.3.10), and 5.0 mL of mixed ICS solution II (5.7.1.2). Dilute to 100 mL with reagent water. ICS solution A must be prepared fresh weekly.

5.6.1.4.2 ICS-AB may be prepared by adding 10.0 mL of mixed ICS solution I (5.7.1.1), 2.0 mL each of 100-μg/mL titanium stock solution (5.3.9) and molybdenum stock solution (5.3.10), 5.0 mL of mixed ICS solution II (5.7.1.2), and 2.0 mL of Mixed ICS solution III (5.7.1.3). Dilute to 100 mL with reagent water. Although the ICS solution AB must be prepared fresh weekly, the analyst should be aware that the solution may precipitate silver more quickly.

5.7 The quality control standard is the initial calibration verification solution (ICV), which must be prepared in the same acid matrix as the calibration standards. This solution must be an independent standard near the midpoint of the linear range at a concentration other than that used for instrument calibration. An independent standard is defined as a standard composed of the analytes from a source different from those used in the standards for instrument calibration.

5.8 Mass spectrometer tuning solution. A solution containing elements representing all of the mass regions of interest (for example, 10 μg/L of Li, Co, In, and Tl) must be prepared to verify that the resolution and mass calibration of the instrument are within the required specifications (see Section 7.5). This solution is also used to verify that the instrument has reached thermal stability (See Section 7.4).

6.0 SAMPLE COLLECTION, PRESERVATION, AND HANDLING

6.1 Sample collection procedures should address the considerations described in Chapter Nine of this Manual.

6.2 See the introductory material in Chapter Three, Inorganic Analytes, Sections 3.1.3 for information on sample handling and preservation. Only polyethylene or fluorocarbon (TFE or PFA) containers are recommended for use in Method 6020.

7.0 PROCEDURE

7.1 Solubilization and digestion procedures are presented in the Sample Preparation Methods (e.g., Methods 3005 - 3051).

7.2 Initiate appropriate operating configuration of the instruments computer according to the instrument manufacturer's instructions.

7.3 Set up the instrument with the proper operating parameters according to the instrument manufacturer's instructions.

7.4 Operating conditions: The analyst should follow the instructions provided by the instrument manufacturer. Allow at least 30 minutes for the instrument to equilibrate before analyzing any samples. This must be verified by analyzing a tuning solution (Section 5.8) at least four times with relative standard deviations of $\leq$ 5% for the analytes contained in the tuning solution.

> NOTE: Precautions must be taken to protect the channel electron multiplier from high ion currents. The channel electron multiplier suffers from fatigue after being exposed to high ion currents. This fatigue can last from several seconds to hours depending on the extent of exposure. During this time period, response factors are constantly changing, which invalidates the calibration curve, causes instability, and invalidates sample analyses.

7.5 Conduct mass calibration and resolution checks in the mass regions of interest. The mass calibration and resolution parameters are required criteria which must be met prior to any samples being analyzed. If the mass calibration differs more than 0.1 amu from the true value, then the mass calibration must be adjusted to the correct value. The resolution must also be verified to be less than 0.9 amu full width at 10 percent peak height.

7.6 Calibrate the instrument for the analytes of interest (recommended isotopes for the analytes in Table 1 are provided in Table 3), using the calibration blank and at least a single initial calibration standard according to the instrument manufacturer's procedure. Flush the system with the rinse blank (5.5.3) between each standard solution. Use the average of at leastthree integrations for both calibration and sample analyses.

7.7 All masses which could affect data quality should be monitored to determine potential effects from matrix components on the analyte peaks. The recommended isotopes to be monitored are liste in Table 3.

7.8 Immediately after the calibration has been established, the calibration must be verified and documented for every analyte by the analysis of the calibration verification solution (Section 5.7). When measurements exceed

± 10% of the accepted value, the analyses must be terminated, the problem corrected, the instrument recalibrated, and the new calibration verified. Any samples analyzed under an out-of-control calibration must be reanalyzed. During the course of an analytical run, the instrument may be "resloped" or recalibrated to correct for instrument drift. A recalibration must then be followed immediately by a new analysis of a CCV and CCB before any further samples may be analyzed.

7.9 Flush the system with the rinse blank solution (5.5.3) until the signal levels return to the method's levels of quantitation (usually about 30 seconds) before the analysis of each sample (see Section 7.7). Nebulize each sample until a steady-state signal is achieved (usually about 30 seconds) prior to collecting data. Analyze the calibration verification solution (Section 5.6) and the calibration blank (Section 5.5.1) at a frequency of at least once every 10 analytical samples. Flow-injection systems may be used as long as they can meet the performance criteria of this method.

7.10 Dilute and reanalyze samples that are more concentrated than the linear range for an analyte (or species needed for a correction) or measure an alternate less-abundant isotope. The linearity at the alternate mass must be confirmed by appropriate calibration (see Sec. 7.6 and 7.8).

7.11 Calculations: The quantitative values shall be reported in appropriate units, such as micrograms per liter (μg/L) for aqueous samples and milligrams per kilogram (mg/kg) for solid samples. If dilutions were performed, the appropriate corrections must be applied to the sample values.

7.11.1 If appropriate, or required, calculate results for solids on a dry-weight basis as follows:

(1) A separate determination of percent solids must be performed.

(2) The concentrations determined in the digest are to be reported on the basis of the dry weight of the sample.

$$\text{Concentration (dry weight)(mg/kg)} = \frac{C \times V}{W \times S}$$

Where,

C = Digest Concentration (mg/L)
V = Final volume in liters after sample preparation
W = Weight in kg of wet sample

$$S = \frac{\%\ \text{Solids}}{100}$$

Calculations should include appropriate interference corrections (see Section 3.2 for examples), internal-standard normalization, and the

summation of signals at 206, 207, and 208 m/z for lead (to compensate for any differences in the abundances of these isotopes between samples and standards).

8.0 QUALITY CONTROL

8.1 All quality control data should be maintained and be available for easy reference or inspection.

8.2 Instrument Detection Limits (IDLs) in µg/L can be estimated by calculating the average of the standard deviations of the three runs on three non-consecutive days from the analysis of a reagent blank solution with seven consecutive measurements per day. Each measurement must be performed as though it were a separate analytical sample (i.e., each measurement must be followed by a rinse and/or any other procedure normally performed between the analysis of separate samples). IDLs must be determined at least every three months and kept with the instrument log book. Refer to Chapter One for additional guidance.

8.3 The intensities of all internal standards must be monitored for every analysis. When the intensity of any internal standard fails to fall between 30 and 120 percent of the intensity of that internal standard in the initial calibration standard, the following procedure is followed. The sample must be diluted fivefold (1+4) and reanalyzed with the addition of appropriate amounts of internal standards. This procedure must be repeated until the internal-standard intensities fall within the prescribed window. The intensity levels of the internal standards for the calibration blank (Section 5.5.1) and instrument check standard (Section 5.6) must agree within ± 20 percent of the intensity level of the internal standard of the original calibration solution. If they do not agree, terminate the analysis, correct the problem, recalibrate, verify the new calibration, and reanalyze the affected samples.

8.4 To obtain analyte data of known quality, it is necessary to measure more than the analytes of interest in order to apply corrections or to determine whether interference corrections are necessary. If the concentrations of interference sources (such as C, Cl, Mo, Zr, W) are such that, at the correction factor, the analyte is less than the limit of quantification and the concentration of interferents are insignificant, then the data may go uncorrected. Note that monitoring the interference sources does not necessarily require monitoring the interferant itself, but that a molecular species may be monitored to indicate the presence of the interferent. When correcttion equations are used, all QC criteria must also be met. Extensive QC for interference corrections are required at all times. The monitored masses must include those elements whose hydrogen, oxygen, hydroxyl, chlorine, nitrogen, carbon and sulfur molecular ions could impact the analytes of interest. Unsuspected interferences may be detected by adding pure major matrix components to a sample to observe any impact on the analyte signals. When an interference source is present, the sample elements impacted must be flagged to indicate (a) the percentage interference correction applied to the data or (b) an uncorrected interference by virtue of the elemental equation used for quantitation. The isotope proportions for an element or molecular-ion cluster provide information useful for quality assurance.

NOTE: Only isobaric elemental, molecular, and doubly charged interference corrections which use the observed isotopic-response ratios or parent-to-oxide ratios (provided an oxide internal standard is used as described in Section 3.2) for each instrument system are acceptable corrections for use in Method 6020.

8.5 Dilution Test: If the analyte concentration is within the linear dynamic range of the instrument and sufficiently high (minimally, a factor of at least 100 times greater than the concentration in the reagent blank, refer to Section 5.5.2), an analysis of a fivefold (1+4) dilution must agree within ± 10% of the original determination. If not, an interference effect must be suspected. One dilution test must be included for each twenty samples (or less) of each matrix in a batch.

8.6 Post-Digestion Spike Addition: An analyte spike added to a portion of a prepared sample, or its dilution, should be recovered to within 75 to 125 percent of the known value or within the laboratory derived acceptance criteria. The spike addition should be based on the indigenous concentration of each element of interest in the sample. If the spike is not recovered within the specified limits, the sample must be diluted and reanalyzed to compensate for the matrix effect. Results must agree to within 10% of the original determination. The use of a standard-addition analysis procedure may also be used to compensate for this effect (Refer to Method 7000).

8.7 A Laboratory Control Sample (LCS) should be analyzed for each analyte using the same sample preparations, analytical methods and QA/QC procedures employed for the test samples. One LCS should be prepared and analyzed for each sample batch at a frequency of one LCS for each 20 samples or less.

8.8 Check the instrument calibration by analyzing appropriate quality control solutions as follows:

8.8.1 Check instrument calibration using a calibration blank (Section 5.5.1) and the initial calibration verification solution (Sections 5.7 and 7.9).

8.8.2 Verify calibration at a frequency of every 10 analytical samples with the instrument check standard (Section 5.6) and the calibration blank (Section 5.5.1). These solutions must also be analyzed for each analyte at the beginning of the analysis and after the last sample.

8.8.3 The results of the initial calibration verification solution and the instrument check standard must agree within ± 10% of the expected value. If not, terminate the analysis, correct the problem, and recalibrate the instrument. Any sample analyzed under an out-of-control calibration must be reanalyzed .

8.8.4 The results of the calibration blank must be less than 3 times the current IDL for each element. If this is not the case, the reason for the out-of-control condition must be found and corrected, and

affected samples must be reanalyzed. If the laboratory consistently ha concentrations greater than 3 times the IDL, the IDL may be indicative of an estimated IDL and should be re-evaluated.

8.9 Verify the magnitude of elemental and molecular-ion isobaric interferences and the adequacy of any corrections at the beginning of an analytical run or once every 12 hours, whichever is more frequent. Do this b analyzing the interference check solutions A and AB. The analyst should be awar that precipitation from solution AB may occur with some elements, specifically silver. Refer to Section 3.0 for a discussion on intereferences and potentia solutions to those intereferences if additional guidance is needed.

8.10 Analyze one duplicate sample for every matrix in a batch at a frequency of one matrix duplicate for every 20 samples.

8.10.1 The relative percent difference (RPD) between duplicate determinations must be calculated as follows:

$$RPD = \frac{|D_1 - D_2|}{(D_1 + D_2)/2} \times 100$$

where:

RPD = relative percent difference.
D_1 = first sample value.
D_2 = second sample value (duplicate)

A control limit of 20% RPD should not be exceeded for analyte values greater than 100 times the instrumental detection limit. If this limit is exceeded, the reason for the out-of-control situation must be found and corrected, and any samples analyzed during the out-of-control condition must be reanalyzed.

9.0 METHOD PERFORMANCE

9.1 In an EPA multi-laboratory study, 10 laboratories applied the ICP-MS technique to both aqueous and solid samples. TABLE 4 summarizes the method performance data for aqueous samples. Performance data for solid samples is provided in TABLE 5.

10.0 REFERENCES

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TABLE 1. ELEMENTS APPROVED FOR ICP-MS DETERMINATION

Element	CAS* #
Aluminum	7429-90-5
Antimony	7440-36-0
Arsenic	7440-38-2
Barium	7440-39-3
Beryllium	7440-41-7
Cadmium	7440-43-9
Chromium	7440-47-3
Cobalt	7440-48-4
Copper	7440-50-8
Lead	7439-92-1
Manganese	7439-96-5
Nickel	7440-02-0
Silver	7440-22-4
Thallium	7440-28-0
Zinc	7440-66-6

TABLE 2. RECOMMENDED INTERFERENCE CHECK SAMPLE COMPONENTS AND CONCENTRATIONS

Solution component	Solution A Concentration (mg/L)	Solution AB Concentration(mg/L)
Al	100.0	100.0
Ca	100.0	100.0
Fe	100.0	100.0
Mg	100.0	100.0
Na	100.0	100.0
P	100.0	100.0
K	100.0	100.0
S	100.0	100.0
C	200.0	200.0
Cl	1000.0	1000.0
Mo	2.0	2.0
Ti	2.0	2.0
As	0.0	0.0200
Cd	0.0	0.0200
Cr	0.0	0.0200
Co	0.0	0.0200
Cu	0.0	0.0200
Mn	0.0	0.0200
Ni	0.0	0.0200
Ag	0.0	0.0200
Zn	0.0	0.0200

TABLE 3. RECOMMENDED ISOTOPES FOR SELECTED ELEMENTS

Mass	Element of interest
27	Aluminum
121, **123**	Antimony
75	Arsenic
138, 137, 136, **135**, 134	Barium
9	Beryllium
209	Bismuth (IS)
114, 112, **111**, 110, 113, 116, 106	Cadmium
42, 43, **44**, 46, 48	Calcium (I)
35, 37, (77, 82)[a]	Chlorine (I)
52, **53**, **50**, 54	Chromium
59	Cobalt
63, **65**	Copper
165	Holmium (IS)
115, 113	Indium (IS)
56, **54**, **57**, 58	Iron (I)
139	Lanthanum (I)
208, **207**, **206**, 204	Lead
6[b], 7	Lithium (IS)
24, **25**, **26**	Magnesium (I)
55	Manganese
98, 96, 92, **97**, 94, (108)[a]	Molybdenum (I)
58, **60**, 62, **61**, 64	Nickel
39	Potassium (I)
103	Rhodium (IS)
45	Scandium (IS)
107, **109**	Silver
23	Sodium (I)
159	Terbium (IS)
205, 203	Thallium
120, **118**	Tin (I)
89	Yttrium (IS)
64, **66**, **68**, **67**, 70	Zinc

NOTE: Method 6020 is recommended for only those analytes listed in Table 1. Other elements are included in this table because they are potential interferents (labeled I) in the determination of recommended analytes, or because they are commonly used internal standards (labeled IS). Isotopes are listed in descending order of natural abundance. The most generally useful isotopes are underlined and in boldface, although certain matrices may require the use of alternative isotopes. [a] These masses are also useful for interference correction (Section 3.2). [b] Internal standard must be enriched in the ^{6}Li isotope. This minimizes interference from indigenous lithium.

TABLE 4. ICP-MS MULTI-LABORATORY PRECISION AND ACCURACY DATA FOR AQUEOUS SOLUTIONS

Element	Comparability[a] Range	%RSD Range	N[b]	S[c]
Aluminum	95 - 100	11 - 14	14 - 14	4
Antimony	d	5.0 - 7.6	16 - 16	3
Arsenic	97 - 114	7.1 - 48	12 - 14	4
Barium	91 - 99	4.3 - 9.0	16 - 16	5
Beryllium	103 - 107	8.6 - 14	13 - 14	3
Cadmium	98 - 102	4.6 - 7.2	18 - 20	3
Calcium	99 - 107	5.7 - 23	17 - 18	5
Chromium	95 - 105	13 - 27	16 - 18	4
Cobalt	101 - 104	8.2 - 8.5	18 - 18	3
Copper	85 - 101	6.1 - 27	17 - 18	5
Iron	91 - 900	11 - 150	10 - 12	5
Lead	71 - 137	11 - 23	17 - 18	6
Magnesium	98 - 102	10 - 15	16 - 16	5
Manganese	95 - 101	8.8 - 15	18 - 18	4
Nickel	98 - 101	6.1 - 6.7	18 - 18	2
Potassium	101 - 114	9.9 - 19	11 - 12	5
Selenium	102 - 107	15 - 25	12 - 12	3
Silver	104 - 105	5.2 - 7.7	13 - 16	2
Sodium	82 - 104	24 - 43	9 - 10	5
Thallium	88 - 97	9.7 - 12	18 - 18	3
Vanadium	107 - 142	23 - 68	8 - 13	3
Zinc	93 - 102	6.8 - 17	16 - 18	5

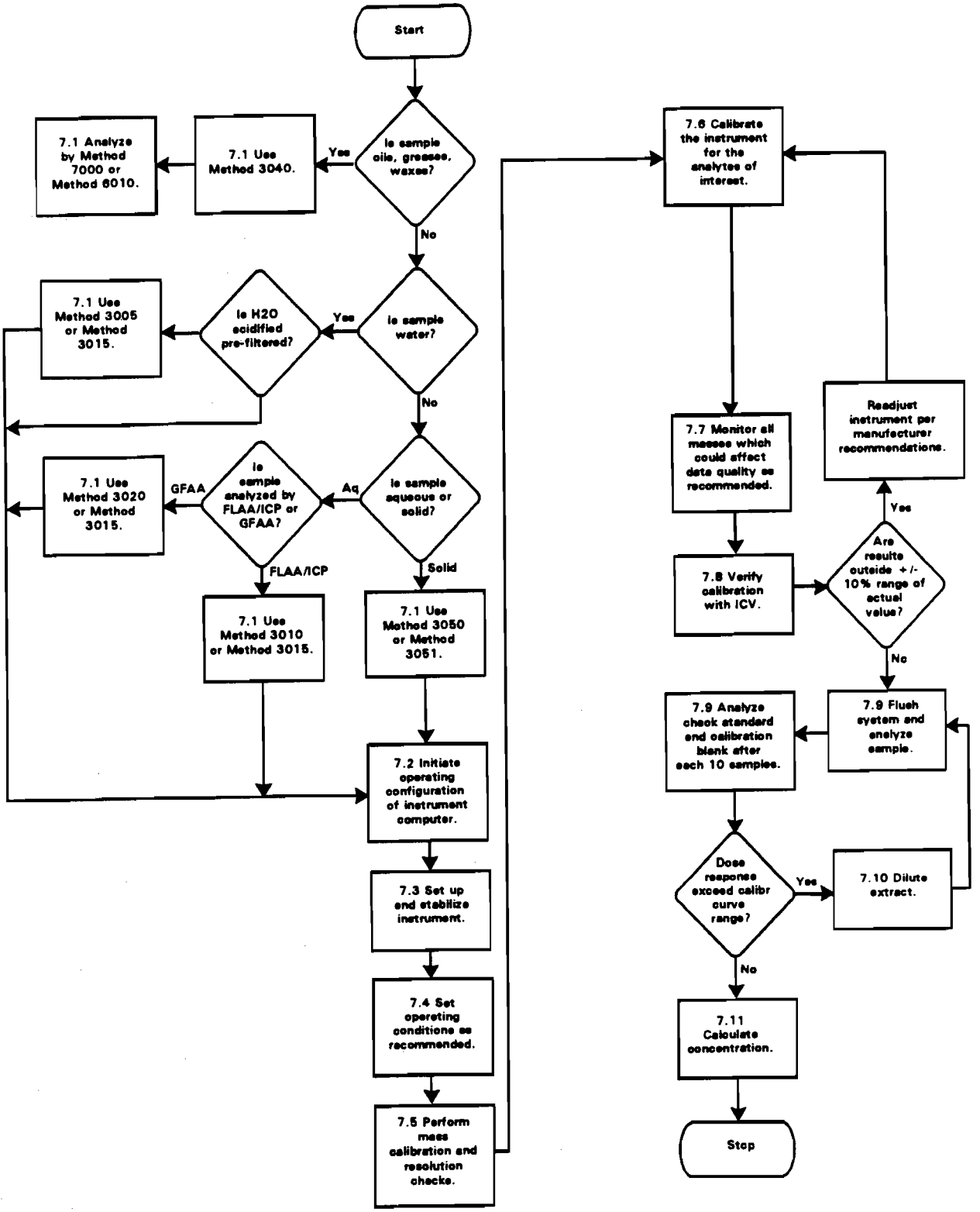
[a] Comparability refers to the percent agreement of mean ICP-MS values to those of the reference technique. [b] N is the range of the number of ICP-MS measurements where the analyte values exceed the limit of quantitation (3.3 times the average IDL value). [c] S is the number of samples with results greater than the limit of quantitation. [d] No comparability values are provided for antimony because of evidence that the reference data is affected by an interference.

TABLE 5. ICP-MS MULTI-LABORATORY PRECISION AND ACCURACY DATA FOR SOLID MATRICES

Element	Comparability[a] Range	%RSD Range	N[b]	S[c]
Aluminum	83 - 101	11 - 39	13 - 14	7
Antimony	d	12 - 21	15 - 16	2
Arsenic	79 - 102	12 - 23	16 - 16	7
Barium	100 - 102	4.3 - 17	15 - 16	7
Beryllium	50 - 87	19 - 34	12 - 14	5
Cadmium	93 - 100	6.2 - 25	19 - 20	5
Calcium	95 - 109	4.1 - 27	15 - 17	7
Chromium	77 - 98	11 - 32	17 - 18	7
Cobalt	43 - 102	15 - 30	17 - 18	6
Copper	90 - 109	9.0 - 25	18 - 18	7
Iron	87 - 99	6.7 - 21	12 - 12	7
Lead	90 - 104	5.9 - 28	15 - 18	7
Magnesium	89 - 111	7.6 - 37	15 - 16	7
Manganese	80 - 108	11 - 40	16 - 18	7
Nickel	87 - 117	9.2 - 29	16 - 18	7
Potassium	97 - 137	11 - 62	10 - 12	5
Selenium	81	39	12	1
Silver	43 - 112	12 - 33	15 - 15	3
Sodium	100 - 146	14 - 77	8 - 10	5
Thallium	91	33	18	1
Vanadium	83 - 147	20 - 70	6 - 14	7
Zinc	84 - 124	14 - 42	18 - 18	7

[a] Comparability refers to the percent agreement of mean ICP-MS values to those of the reference technique. [b] N is the range of the number of ICP-MS measurements where the analyte values exceed the limit of quantitation (3.3 times the average IDL value). [c] S is the number of samples with results greater than the limit of quantitation. [d] No comparability values are provided for antimony because of evidence that the reference data is affected by an interference.

METHOD 6020
INDUCTIVELY COUPLED PLASMA - MASS SPECTROMETRY



METHOD 7000A

ATOMIC ABSORPTION METHODS

1.0 SCOPE AND APPLICATION

1.1 Metals in solution may be readily determined by atomic absorption spectroscopy. The method is simple, rapid, and applicable to a large number of metals in drinking, surface, and saline waters and domestic and industrial wastes. While drinking water free of particulate matter may be analyzed directly, ground water, other aqueous samples, EP extracts, industrial wastes, soils, sludges, sediments, and other solid wastes require digestion prior to analysis for both total and acid leachable metals. Analysis for dissolved elements does not require digestion if the sample has been filtered and acidified.

1.2 Detection limits, sensitivity, and optimum ranges of the metals will vary with the matrices and models of atomic absorption spectrophotometers. The data shown in Table 1 provide some indication of the detection limits obtainable by direct aspiration and by furnace techniques. For clean aqueous samples, the detection limits shown in the table by direct aspiration may be extended downward with scale expansion and upward by using a less sensitive wavelength or by rotating the burner head. Detection limits by direct aspiration may also be extended through concentration of the sample and/or through solvent extraction techniques. For certain samples, lower concentrations may also be determined using the furnace techniques. The detection limits given in Table 1 are somewhat dependent on equipment (such as the type of spectrophotometer and furnace accessory, the energy source, the degree of electrical expansion of the output signal), and are greatly dependent on sample matrix. Detection limits should be established, empirically, for each matrix type analyzed. When using furnace techniques, however, the analyst should be cautioned as to possible chemical reactions occurring at elevated temperatures which may result in either suppression or enhancement of the analysis element. To ensure valid data with furnace techniques, the analyst must examine each matrix for interference effects (see Step 3.2.1) and, if detected, treat them accordingly, using either successive dilution, matrix modification, or method of standard additions (see Step 8.7).

1.3 Where direct-aspiration atomic absorption techniques do not provide adequate sensitivity, reference is made to specialized procedures (in addition to the furnace procedure) such as the gaseous-hydride method for arsenic and selenium and the cold-vapor technique for mercury.

2.0 SUMMARY OF METHOD

2.1 Although methods have been reported for the analysis of solids by atomic absorption spectroscopy, the technique generally is limited to metals in solution or solubilized through some form of sample processing.

2.2 Preliminary treatment of waste water, ground water, EP extracts, and industrial waste is always necessary because of the complexity and variability of sample matrix. Solids, slurries, and suspended material must be subjected to a solubilization process before analysis. This process may vary because of the

metals to be determined and the nature of the sample being analyzed. Solubilization and digestion procedures are presented in Step 3.2 (Sample Preparation Methods).

2.3 In direct-aspiration atomic absorption spectroscopy, a sample is aspirated and atomized in a flame. A light beam from a hollow cathode lamp or an electrodeless discharge lamp is directed through the flame into a monochromator, and onto a detector that measures the amount of absorbed light. Absorption depends upon the presence of free unexcited ground-state atoms in the flame. Because the wavelength of the light beam is characteristic of only the metal being determined, the light energy absorbed by the flame is a measure of the concentration of that metal in the sample. This principle is the basis of atomic absorption spectroscopy.

2.4 When using the furnace technique in conjunction with an atomic absorption spectrophotometer, a representative aliquot of a sample is placed in the graphite tube in the furnace, evaporated to dryness, charred, and atomized. As a greater percentage of available analyte atoms is vaporized and dissociated for absorption in the tube rather than the flame, the use of smaller sample volumes or detection of lower concentrations of elements is possible. The principle is essentially the same as with direct aspiration atomic absorption, except that a furnace, rather than a flame, is used to atomize the sample. Radiation from a given excited element is passed through the vapor containing ground-state atoms of that element. The intensity of the transmitted radiation decreases in proportion to the amount of the ground-state element in the vapor. The metal atoms to be measured are placed in the beam of radiation by increasing the temperature of the furnace, thereby causing the injected specimen to be volatilized. A monochromator isolates the characteristic radiation from the hollow cathode lamp or electrodeless discharge lamp, and a photosensitive device measures the attenuated transmitted radiation.

3.0 INTERFERENCES

3.1 Direct aspiration

3.1.1 The most troublesome type of interference in atomic absorption spectrophotometry is usually termed "chemical" and is caused by lack of absorption of atoms bound in molecular combination in the flame. This phenomenon can occur when the flame is not sufficiently hot to dissociate the molecule, as in the case of phosphate interference with magnesium, or when the dissociated atom is immediately oxidized to a compound that will not dissociate further at the temperature of the flame. The addition of lanthanum will overcome phosphate interference in magnesium, calcium, and barium determinations. Similarly, silica interference in the determination of manganese can be eliminated by the addition of calcium.

3.1.2 Chemical interferences may also be eliminated by separating the metal from the interfering material. Although complexing agents are employed primarily to increase the sensitivity of the analysis, they may also be used to eliminate or reduce interferences.

3.1.3 The presence of high dissolved solids in the sample may result in an interference from nonatomic absorbance such as light scattering. If background correction is not available, a nonabsorbing wavelength should be checked. Preferably, samples containing high solids should be extracted.

3.1.4 Ionization interferences occur when the flame temperature is sufficiently high to generate the removal of an electron from a neutral atom, giving a positively charged ion. This type of interference can generally be controlled by the addition, to both standard and sample solutions, of a large excess (1,000 mg/L) of an easily ionized element such as K, Na, Li or Cs.

3.1.5 Spectral interference can occur when an absorbing wavelength of an element present in the sample but not being determined falls within the width of the absorption line of the element of interest. The results of the determination will then be erroneously high, due to the contribution of the interfering element to the atomic absorption signal. Interference can also occur when resonant energy from another element in a multielement lamp, or from a metal impurity in the lamp cathode, falls within the bandpass of the slit setting when that other metal is present in the sample. This type of interference may sometimes be reduced by narrowing the slit width.

3.1.6 Samples and standards should be monitored for viscosity differences that may alter the aspiration rate.

3.1.7 All metals are not equally stable in the digestate, especially if it contains only nitric acid, not nitric acid and hydrochloric acid. The digestate should be analyzed as soon as possible, with preference given to Sn, Sb, Mo, Ba, and Ag.

3.2 Furnace procedure

3.2.1 Although the problem of oxide formation is greatly reduced with furnace procedures because atomization occurs in an inert atmosphere, the technique is still subject to chemical interferences. The composition of the sample matrix can have a major effect on the analysis. It is those effects which must be determined and taken into consideration in the analysis of each different matrix encountered. To help verify the absence of matrix or chemical interference, the serial dilution technique (see Step 8.6) may be used. Those samples which indicate the presence of interference should be treated in one or more of the following ways:

1. Successively dilute and reanalyze the samples to eliminate interferences.

2. Modify the sample matrix either to remove interferences or to stabilize the analyte. Examples are the addition of ammonium nitrate to remove alkali chlorides and the addition of ammonium phosphate to retain cadmium. The mixing of hydrogen with the inert purge gas has also been used to suppress chemical interference. The hydrogen acts as a reducing agent and aids in molecular dissociation.

3. Analyze the sample by method of standard additions while noticing the precautions and limitations of its use (see Step 8.7.2).

3.2.2 Gases generated in the furnace during atomization may have molecular absorption bands encompassing the analytical wavelength. When this occurs, use either background correction or choose an alternate wavelength. Background correction may also compensate for nonspecific broad-band absorption interference.

3.2.3 Continuum background correction cannot correct for all types of background interference. When the background interference cannot be compensated for, chemically remove the analyte or use an alternate form of background correction, e.g., Zeeman background correction.

3.2.4 Interference from a smoke-producing sample matrix can sometimes be reduced by extending the charring time at a higher temperature or utilizing an ashing cycle in the presence of air. Care must be taken, however, to prevent loss of the analyte.

3.2.5 Samples containing large amounts of organic materials should be oxidized by conventional acid digestion before being placed in the furnace. In this way, broad-band absorption will be minimized.

3.2.6 Anion interference studies in the graphite furnace indicate that, under conditions other than isothermal, the nitrate anion is preferred. Therefore, nitric acid is preferable for any digestion or solubilization step. If another acid in addition to nitric acid is required, a minimum amount should be used. This applies particularly to hydrochloric and, to a lesser extent, to sulfuric and phosphoric acids.

3.2.7 Carbide formation resulting from the chemical environment of the furnace has been observed. Molybdenum may be cited as an example. When carbides form, the metal is released very slowly from the resulting metal carbide as atomization continues. Molybdenum may require 30 seconds or more atomization time before the signal returns to baseline levels. Carbide formation is greatly reduced and the sensitivity increased with the use of pyrolytically coated graphite. Elements that readily form carbides are noted with the symbol (p) in Table 1.

3.2.8 For comments on spectral interference, see Step 3.1.5.

3.2.9 Cross-contamination and contamination of the sample can be major sources of error because of the extreme sensitivities achieved with the furnace. The sample preparation work area should be kept scrupulously clean. All glassware should be cleaned as directed in Step 4.8. Pipet tips are a frequent source of contamination. If suspected, they should be acid soaked with 1:5 nitric acid and rinsed thoroughly with tap and reagent water. The use of a better grade of pipet tip can greatly reduce this problem. Special attention should be given to reagent blanks in both analysis and in the correction of analytical results. Lastly, pyrolytic graphite, because of the production process and handling, can become contaminated. As many as five to ten high-temperature burns may be required to clean the tube before use.

4.0 APPARATUS AND MATERIALS

4.1 Atomic absorption spectrophotometer - Single- or dual-channel, single- or double-beam instrument having a grating monochromator, photomultiplier detector, adjustable slits, a wavelength range of 190 to 800 nm, and provisions for interfacing with a graphical display.

4.2 Burner - The burner recommended by the particular instrument manufacturer should be used. For certain elements the nitrous oxide burner is required.

4.3 Hollow cathode lamps - Single-element lamps are preferred but multielement lamps may be used. Electrodeless discharge lamps may also be used when available. Other types of lamps meeting the performance criteria of this method may be used.

4.4 Graphite furnace - Any furnace device capable of reaching the specified temperatures is satisfactory.

4.5 Graphical display and recorder - A recorder is recommended for furnace work so that there will be a permanent record and that any problems with the analysis such as drift, incomplete atomization, losses during charring, changes in sensitivity, peak shape, etc., can be easily recognized.

4.6 Pipets - Microliter, with disposable tips. Sizes can range from 5 to 100 uL as required. Pipet tips should be checked as a possible source of contamination prior to their use. The accuracy of automatic pipets must be verified daily. Class A pipets can be used for the measurement of volumes larger than 1 mL.

4.7 Pressure-reducing valves - The supplies of fuel and oxidant should be maintained at pressures somewhat higher than the controlled operating pressure of the instrument by suitable valves.

4.8 Glassware - All glassware, polypropylene, or Teflon containers, including sample bottles, flasks and pipets, should be washed in the following sequence: detergent, tap water, 1:1 nitric acid, tap water, 1:1 hydrochloric acid, tap water, and reagent water. (Chromic acid should not be used as a cleaning agent for glassware if chromium is to be included in the analytical scheme.) If it can be documented through an active analytical quality control program using spiked samples and reagent blanks that certain steps in the cleaning procedure are not required for routine samples, those steps may be eliminated from the procedure.

5.0 REAGENTS

5.1 Reagent grade chemicals shall be used in all tests. Unless otherwise indicated, it is intended that all reagents shall conform to the specifications of the Committee on Analytical Reagents of the American Chemical Society, where such specifications are available. Other grades may be used, provided it is first ascertained that the reagent is of sufficiently high purity to permit its use

without lessening the accuracy of the determination. All reagents should be analyzed to provide proof that all constituents are below the MDLs.

5.2 Reagent water. All references to water in this method refer to reagent water unless otherwise specified. Reagent grade water will be of at least 16 Mega Ohm quality.

5.3 Nitric acid (concentrated), HNO_3. Use a spectrograde acid certified for AA use. Prepare a 1:1 dilution with water by adding the concentrated acid to an equal volume of water. If the reagent blank is less than the IDL, the acid may be used.

5.4 Hydrochloric acid (1:1), HCl. Use a spectrograde acid certified for AA use. Prepare a 1:1 dilution with water by adding the concentrated acid to an equal volume of water. If the reagent blank is less than the IDL, the acid may be used.

5.5 Fuel and oxidant - High purity acetylene is generally acceptable. Air may be supplied from a compressed air line, a laboratory compressor, or a cylinder of compressed air and should be clean and dry. Nitrous oxide is also required for certain determinations. Standard, commercially available argon and nitrogen are required for furnace work.

5.6 Stock standard metal solutions - Stock standard solutions are prepared from high purity metals, oxides, or nonhygroscopic salts using water and redistilled nitric or hydrochloric acids. (See individual methods for specific instructions.) Sulfuric or phosphoric acids should be avoided as they produce an adverse effect on many elements. The stock solutions are prepared at concentrations of 1,000 mg of the metal per liter. Commercially available standard solutions may also be used. Where the sample viscosity, surface tension, and components cannot be accurately matched with standards, the method of standard addition (MSA) may be used (see Step 8.7).

5.7 Calibration standards - For those instruments which do not read out directly in concentration, a calibration curve is prepared to cover the appropriate concentration range. Usually, this means the preparation of standards which produce an absorbance of 0.0 to 0.7. Calibration standards are prepared by diluting the stock metal solutions at the time of analysis. For best results, calibration standards should be prepared fresh each time a batch of samples is analyzed. Prepare a blank and at least three calibration standards in graduated amounts in the appropriate range of the linear part of the curve. The calibration standards should be prepared using the same type of acid or combination of acids and at the same concentration as will result in the samples following processing. Beginning with the blank and working toward the highest standard, aspirate the solutions and record the readings. Repeat the operation with both the calibration standards and the samples a sufficient number of times to secure a reliable average reading for each solution. Calibration standards for furnace procedures should be prepared as described on the individual sheets for that metal. Calibration curves are always required.

6.0 SAMPLE COLLECTION, PRESERVATION, AND HANDLING

6.1 See the introductory material in Chapter Three, Metallic Analytes.

7.0 PROCEDURE

7.1 Preliminary treatment of waste water, ground water, EP extracts, and industrial waste is always necessary because of the complexity and variability of sample matrices. Solids, slurries, and suspended material must be subjected to a solubilization process before analysis. This process may vary because of the metals to be determined and the nature of the sample being analyzed. Solubilization and digestion procedures are presented in Chapter Three, Step 3.2, Sample Preparation Methods. Samples which are to be analyzed for dissolved constituents need not be digested if they have been filtered and acidified.

7.2 Direct aspiration (flame) procedure

7.2.1 Differences between the various makes and models of satisfactory atomic absorption spectrophotometers prevent the formulation of detailed instructions applicable to every instrument. The analyst should follow the manufacturer's operating instructions for a particular instrument. In general, after choosing the proper lamp for the analysis, allow the lamp to warm up for a minimum of 15 minutes, unless operated in a double-beam mode. During this period, align the instrument, position the monochromator at the correct wavelength, select the proper monochromator slit width, and adjust the current according to the manufacturer's recommendation. Subsequently, light the flame and regulate the flow of fuel and oxidant. Adjust the burner and nebulizer flow rate for maximum percent absorption and stability. Balance the photometer. Run a series of standards of the element under analysis. Construct a calibration curve by plotting the concentrations of the standards against absorbances. Set the curve corrector of a direct reading instrument to read out the proper concentration. Aspirate the samples and determine the concentrations either directly or from the calibration curve. Standards must be run each time a sample or series of samples is run.

7.3 Furnace procedure

7.3.1 Furnace devices (flameless atomization) are a most useful means of extending detection limits. Because of differences between various makes and models of satisfactory instruments, no detailed operating instructions can be given for each instrument. Instead, the analyst should follow the instructions provided by the manufacturer of a particular instrument.

7.3.2 Background correction is important when using flameless atomization, especially below 350 nm. Certain samples, when atomized, may absorb or scatter light from the lamp. This can be caused by the presence of gaseous molecular species, salt particles, or smoke in the sample beam. If no correction is made, sample absorbance will be greater than it should be, and the analytical result will be erroneously high. Zeeman background correction is effective in overcoming composition or structured background

interferences. It is particularly useful when analyzing for As in the presence of Al and when analyzing for Se in the presence of Fe.

7.3.3 Memory effects occur when the analyte is not totally volatilized during atomization. This condition depends on several factors: volatility of the element and its chemical form, whether pyrolytic graphite is used, the rate of atomization, and furnace design. This situation is detected through blank burns. The tube should be cleaned by operating the furnace at full power for the required time period, as needed, at regular intervals during the series of determinations.

7.3.4 Inject a measured microliter aliquot of sample into the furnace and atomize. If the concentration found is greater than the highest standard, the sample should be diluted in the same acid matrix and reanalyzed. The use of multiple injections can improve accuracy and help detect furnace pipetting errors.

7.3.5 To verify the absence of interference, follow the serial dilution procedure given in Step 8.6.

7.3.6 A check standard should be run after approximately every 10 sample injections. Standards are run in part to monitor the life and performance of the graphite tube. Lack of reproducibility or significant change in the signal for the standard indicates that the tube should be replaced. Tube life depends on sample matrix and atomization temperature. A conservative estimate would be that a tube will last at least 50 firings. A pyrolytic coating will extend that estimated life by a factor of three.

7.4 Calculation

7.4.1 For determination of metal concentration by direct aspiration and furnace: Read the metal value from the calibration curve or directly from the read-out system of the instrument.

7.4.2 If dilution of sample was required:

$$\text{ug/L metal in sample} = A\left(\frac{C + B}{C}\right)$$

where:

A = ug/L of metal in diluted aliquot from calibration curve.
B = Acid blank matrix used for dilution, mL.
C = Sample aliquot, mL.

7.4.3 For solid samples, report all concentrations in consistent units based on wet weight. Hence:

$$\text{ug metal/kg sample} = \frac{A \times V}{W}$$

where:

A = ug/L of metal in processed sample from calibration curve.
V = Final volume of the processed sample, mL.
W = Weight of sample, grams.

7.4.4 Different injection volumes must not be used for samples and standards. Instead, the sample should be diluted and the same size injection volume be used for both samples and standards. If dilution of the sample was required:

$$\text{ug/L of metal in sample} = Z \left(\frac{C + B}{C} \right)$$

where:

Z = ug/L of metal read from calibration curve or read-out system.
B = Acid blank matrix used for dilution mL.
C = Sample aliquot, mL.

8.0 QUALITY CONTROL

8.1 All quality control data should be maintained and available for easy reference or inspection.

8.2 A calibration curve must be prepared each day with a minimum of a calibration blank and three standards. After calibration, the calibration curve must be verified by use of at least a calibration blank and a calibration check standard (made from a reference material or other independent standard material) at or near the mid-range. The calibration reference standard must be measured within 10 % of it's true value for the curve to be considered valid.

8.3 If more than 10 samples per day are analyzed, the working standard curve must be verified by measuring satisfactorily a mid-range standard or reference standard after every 10 samples. This sample value must be within 20% of the true value, or the previous ten samples need to be reanalyzed.

8.4 At least one matrix spike and one matrix spike duplicate sample shall be included in each analytical batch. A laboratory control sample shall also be processed with each sample batch. Refer to Chapter One for more information.

8.5 Where the sample matrix is so complex that viscosity, surface tension, and components cannot be accurately matched with standards, the method of standard addition (MSA) is recommended (see Section 8.7 below). Section 8.6 provides tests to evaluate the need for using the MSA.

8.6 Interference tests

8.6.1 Dilution test - For each analytical batch select one typical sample for serial dilution to determine whether interferences are present. The concentration of the analyte should be at least 25 times the estimated detection limit. Determine the apparent concentration in the undiluted sample. Dilute the sample by a minimum of five fold (1+4) and reanalyze. If all of the samples in the batch are below 10 times the detection limits, perform the spike recovery analysis described below. Agreement within 10% between the concentration for the undiluted sample and five times the concentration for the diluted sample indicates the absence of interferences, and such samples may be analyzed without using the method of standard additions.

8.6.2 Recovery test - If results from the dilution test do not agree, a matrix interference may be suspected and a spiked sample should be analyzed to help confirm the finding from the dilution test. Withdraw another aliquot of the test sample and add a known amount of analyte to bring the concentration of the analyte to 2 to 5 times the original concentration. If all of the samples in the batch have analyte concentrations below the detection limit, spike the selected sample at 20 times the detection limit. Analyze the spiked sample and calculate the spike recovery. If the recovery is less than 85% or greater than 115%, the method of standard additions shall be used for all samples in the batch.

8.7 Method of standard additions - The standard addition technique involves adding known amounts of standard to one or more aliquots of the processed sample solution. This technique compensates for a sample constituent that enhances or depresses the analyte signal, thus producing a different slope from that of the calibration standards. It will not correct for additive interferences which cause a baseline shift. The method of standard additions shall be used for analysis of all EP extracts, on all analyses submitted as part of a delisting petition, and whenever a new sample matrix is being analyzed.

8.7.1 The simplest version of this technique is the single-addition method, in which two identical aliquots of the sample solution, each of volume V_x, are taken. To the first (labeled A) is added a known volume V_s of a standard analyte solution of concentration C_s. To the second aliquot (labeled B) is added the same volume V_s of the solvent. The analytical signals of A and B are measured and corrected for nonanalyte signals. The unknown sample concentration C_x is calculated:

$$C_x = \frac{S_B V_s C_s}{(S_A - S_B) V_x}$$

where S_A and S_B are the analytical signals (corrected for the blank) of solutions A and B, respectively. V_s and C_s should be chosen so that S_A is roughly twice S_B on the average, avoiding excess dilution of the sample. If a separation or concentration step is used, the additions are best made first and carried through the entire procedure.

8.7.2 Improved results can be obtained by employing a series of standard additions. To equal volumes of the sample are added a series of standard solutions containing different known quantities of the analyte, and all solutions are diluted to the same final volume. For example, addition 1 should be prepared so that the resulting concentration is approximately 50 percent of the expected absorbance from the endogenous analyte in the sample. Additions 2 and 3 should be prepared so that the concentrations are approximately 100 and 150 percent of the expected endogenous sample absorbance. The absorbance of each solution is determined and then plotted on the vertical axis of a graph, with the concentrations of the known standards plotted on the horizontal axis. When the resulting line is extrapolated to zero absorbance, the point of interception of the abscissa is the endogenous concentration of the analyte in the sample. The abscissa on the left of the ordinate is scaled the same as on the right side, but in the opposite direction from the

ordinate. An example of a plot so obtained is shown in Figure 1. A linear regression program may be used to obtain the intercept concentration.

8.7.3 For the results of this MSA technique to be valid, the following limitations must be taken into consideration:

1. The apparent concentrations from the calibration curve must be linear over the concentration range of concern. For the best results, the slope of the MSA plot should be nearly the same as the slope of the standard curve. If the slope is significantly different (greater than 20%), caution should be exercised.

2. The effect of the interference should not vary as the ratio of analyte concentration to sample matrix changes, and the standard addition should respond in a similar manner as the analyte.

3. The determination must be free of spectral interference and corrected for nonspecific background interference.

8.8 All quality control measures described in Chapter One should be followed.

9.0 METHOD PERFORMANCE

9.1 See individual methods.

10.0 REFERENCES

1. Methods for Chemical Analysis of Water and Wastes; U.S. Environmental Protection Agency. Office of Research and Development. Environmental Monitoring and Support Laboratory. ORD Publication Offices of Center for Environmental Research Information: Cincinnati, OH, 1983; EPA-600/4-79-020.

2. Rohrbough, W.G.; et al. Reagent Chemicals, American Chemical Society Specifications, 7th ed.; American Chemical Society: Washington, DC, 1986.

3. 1985 Annual Book of ASTM Standards, Vol. 11.01; "Standard Specification for Reagent Water"; ASTM: Philadelphia, PA, 1985; D1193-77.

TABLE 1.
ATOMIC ABSORPTION CONCENTRATION RANGES

Metal	Direct Aspiration		Furnace Procedure[a,c]
	Detection Limit (mg/L)	Sensitivity (mg/L)	Detection Limit (ug/L)
Aluminum	0.1	1	--
Antimony	0.2	0.5	3
Arsenic[b]	0.002	--	1
Barium	0.1	0.4	2
Beryllium	0.005	0.025	0.2
Cadmium	0.005	0.025	0.1
Calcium	0.01	0.08	--
Chromium	0.05	0.25	1
Cobalt	0.05	0.2	1
Copper	0.02	0.1	1
Iron	0.03	0.12	1
Lead	0.1	0.5	1
Lithium	0.002	0.04	--
Magnesium	0.001	0.007	--
Manganese	0.01	0.05	0.2
Mercury[d]	0.0002	--	--
Molybdenum(p)	0.1	0.4	1
Nickel	0.04	0.15	--
Osmium	0.03	1	--
Potassium	0.01	0.04	--
Selenium[b]	0.002	--	2
Silver	0.01	0.06	0.2
Sodium	0.002	0.015	--
Strontium	0.03	0.15	--
Thallium	0.1	0.5	1
Tin	0.8	4	--
Vanadium(p)	0.2	0.8	4
Zinc	0.005	0.02	0.05

NOTE: The symbol (p) indicates the use of pyrolytic graphite with the furnace procedure.

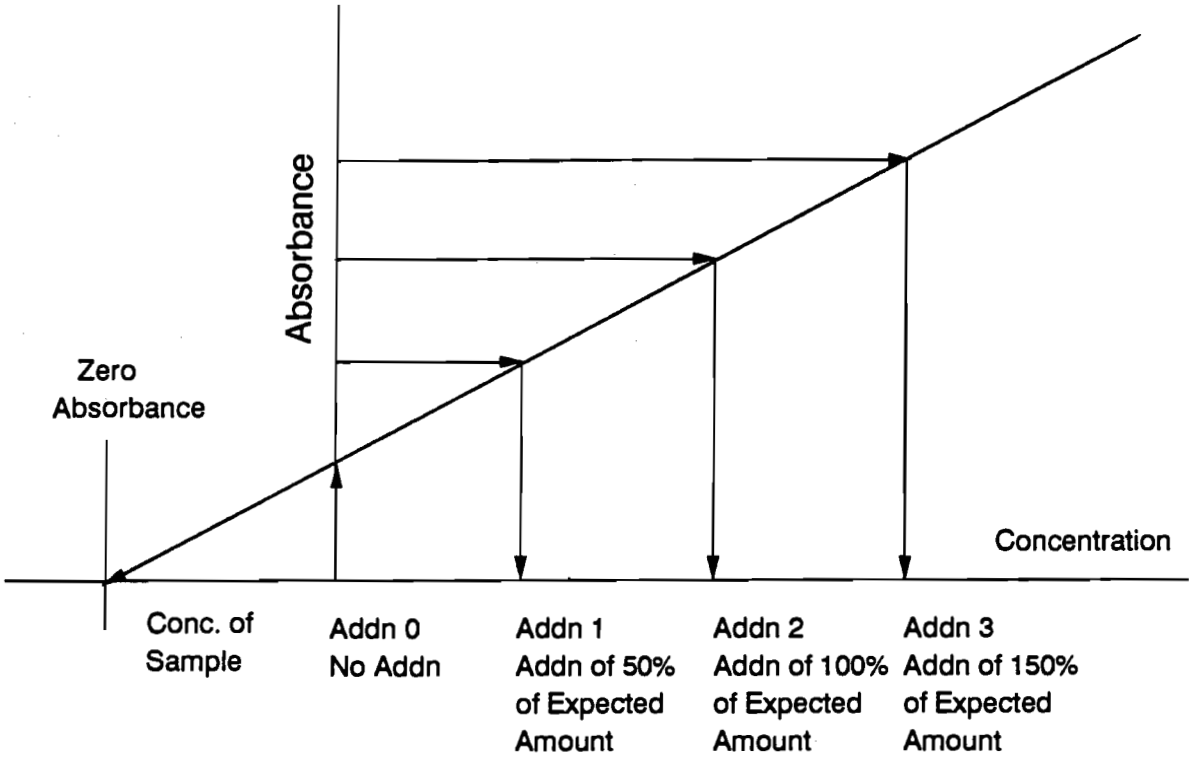
[a]For furnace sensitivity values, consult instrument operating manual.

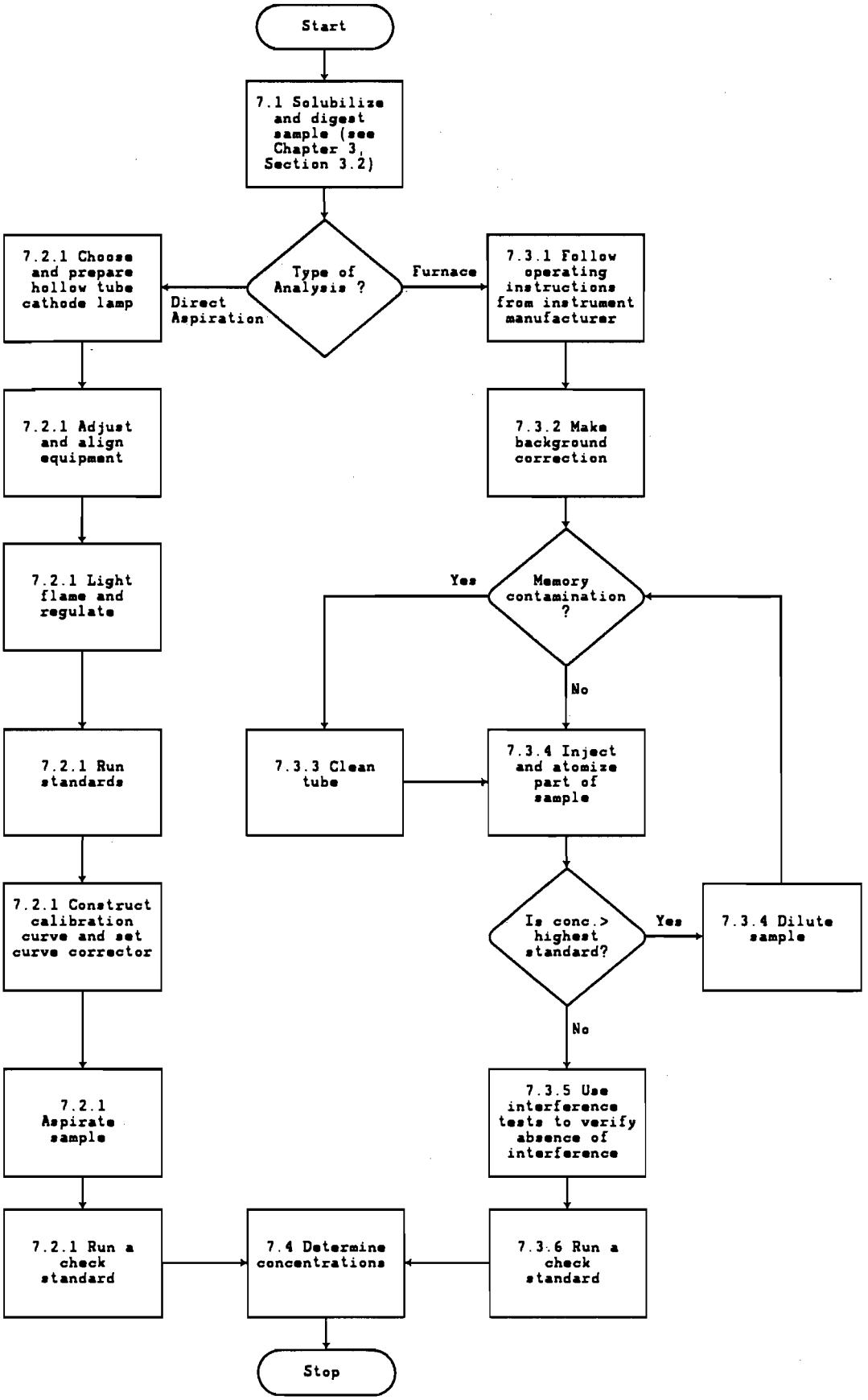
[b]Gaseous hydride method.

[c]The listed furnace values are those expected when using a 20-uL injection and normal gas flow, except in the cases of arsenic and selenium, where gas interrupt is used.

[d]Cold vapor technique.

FIGURE 1.
STANDARD ADDITION PLOT




Start
7.1 Solubilize and digest sample (see Chapter 3, Section 3.2)
Type of Analysis ?
Direct Aspiration
Furnace
7.2.1 Choose and prepare hollow tube cathode lamp
7.3.1 Follow operating instructions from instrument manufacturer
7.2.1 Adjust and align equipment
7.3.2 Make background correction
7.2.1 Light flame and regulate
Memory contamination ?
Yes
No
7.2.1 Run standards
7.3.3 Clean tube
7.3.4 Inject and atomize part of sample
7.2.1 Construct calibration curve and set curve corrector
Is conc.> highest standard?
Yes
7.3.4 Dilute sample
No
7.2.1 Aspirate sample
7.3.5 Use interference tests to verify absence of interference
7.2.1 Run a check standard
7.4 Determine concentrations
7.3.6 Run a check standard
Stop

METHOD 7020

ALUMINUM (ATOMIC ABSORPTION, DIRECT ASPIRATION)

1.0 SCOPE AND APPLICATION

1.1 See Section 1.0 of Method 7000

2.0 SUMMARY OF METHOD

2.1 See Section 2.0 of Method 7000.

3.0 INTERFERENCES

3.1 See Section 3.0 of Method 7000 if interferences are suspected.

3.2 Aluminum may be as much as 15% ionized in a nitrous-oxide/acetylene flame. Use of an ionization suppressor (1,000 ug/mL K as KCl) as in Method 7000, Paragraph 3.1.4, will eliminate this interference.

3.3 Aluminum is a very common contaminant, and great care should be taken to avoid contamination.

4.0 APPARATUS AND MATERIALS

4.1 For basic apparatus, see Section 4.0 of Method 7000.

4.2 Instrument parameters (general):

4.2.1 Aluminum hollow cathode lamp.
4.2.2 Wavelength: 324.7 nm.
4.2.3 Fuel: Acetylene.
4.2.4 Oxidant: Nitrous oxide.
4.2.5 Type of flame: Fuel rich.
4.2.6 Background correction: Not required.

5.0 REAGENTS

5.1 See Section 5.0 of Method 7000.

5.2 Preparation of standards:

5.2.1 Stock solution: Dissolve 1.000 g of aluminum metal in dilute HCl with gentle warming. Dilute to 1 liter with Type II water. Alternatively, procure a certified standard from a supplier and verify by comparison with a second standard.

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5.2.2 Prepare dilutions of the stock solution to be used as calibration standards at the time of analysis. The calibration standards should be prepared using the same type of acid and at the same concentration as will result in the sample to be analyzed after processing. Samples and standards should also contain 2 mL KCl/100 mL solution (Paragraph 3.2 above).

5.3 Potassium chloride solution: Dissolve 95 g potassium chloride (KCl) in Type II water and dilute to 1 liter.

6.0 SAMPLE COLLECTION, PRESERVATION, AND HANDLING

6.1 See Chapter Three, Section 3.1.3, Sample Handling and Preservation.

7.0 PROCEDURE

7.1 Sample preparation: The procedures for preparation of the sample are given in Chapter Three, Section 3.2.

8.0 QUALITY CONTROL

8.1 See Section 8.0 of Method 7000.

9.0 METHOD PERFORMANCE

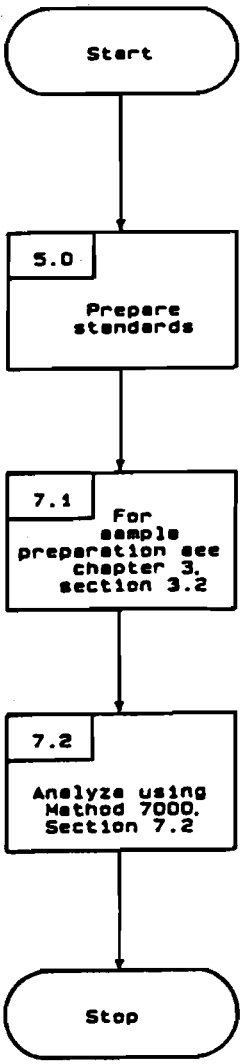
9.1 Precision and accuracy data are available in Method 202.1 of Methods for Chemical Analysis of Water and Wastes.

9.2 The performance characteristics for an aqueous sample free of interferences are:

Optimum concentration range: 5-50 mg/L, with a wavelength of 309.3 nm.
Sensitivity: 1 mg/L.
Detection limit: 0.1 mg/L.

10.0 REFERENCES

1. Methods for Chemical Analysis of Water and Wastes, EPA-600/4-82-055, Method 202.1, December 1982.


Start
5.0
Prepare standards
7.1
For sample preparation see chapter 3, section 3.2
7.2
Analyze using Method 7000, Section 7.2
Stop

METHOD 7040

ANTIMONY (ATOMIC ABSORPTION, DIRECT ASPIRATION)

1.0 SCOPE AND APPLICATION

1.1 See Section 1.0 of Method 7000

2.0 SUMMARY OF METHOD

2.1 See Section 2.0 of Method 7000.

3.0 INTERFERENCES

3.1 See Section 3.0 of Method 7000 if interferences are suspected.

3.2 In the presence of lead (1,000 mg/L), a spectral interference may occur at the 217.6-nm resonance line. In this case, the 231.1-nm antimony line should be used.

3.3 Increasing the acid concentrations decreases the antimony absorption. To avoid this effect, the acid concentration in the samples and in the standards should be matched.

3.4 Excess concentrations of copper and nickel (and possibly other elements), as well as acids, can interfere with antimony analyses. If the sample contains these matrix types, either matrices of the standards should be matched to those of the sample or the sample should be analyzed using a nitrous oxide/acetylene flame.

4.0 APPARATUS AND MATERIALS

4.1 For basic apparatus, see Section 4.0 of Method 7000.

4.2 Instrument parameters (general):

4.2.1 **Antimony hollow cathode lamp or electrodeless discharge lamp.**
4.2.2 **Wavelength:** 217.6 nm (primary); 231.1 nm (secondary).
4.2.3 **Fuel:** Acetylene.
4.2.4 **Oxidant:** Air.
4.2.5 **Type of flame:** Fuel lean.
4.2.6 **Background correction:** Required.

5.0 REAGENTS

5.1 See Section 5.0 of Method 7000.

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5.2 Preparation of standards:

5.2.1 **Stock solution:** Carefully weigh 2.7426 g of antimony potassium tartrate, $K(SbO)C_4H_4O_6 \cdot 1/2H_2O$ (analytical reagent grade), and dissolve in Type II water. Dilute to 1 liter with Type II water; 1 mL = 1 mg Sb (1,000 mg/L). Alternatively, procure a certified standard from a supplier and verify by comparison with a second standard.

5.2.2 Prepare dilutions of the stock solution to be used as calibration standards at the time of analysis. The calibration standards should contain 0.2% (v/v) HNO_3 and 1-2% v/v HCl, prepared using the same types of acid and at the same concentrations as in the sample after processing.

6.0 SAMPLE COLLECTION, PRESERVATION, AND HANDLING

6.1 See Chapter Three, Section 3.1.3, Sample Handling and Preservation.

7.0 PROCEDURE

7.1 Sample preparation: The procedures for preparation of the sample are given in Method 3005. Method 3005, a soft digestion, is presently the only digestion procedure recommended for Sb. It yields better recoveries than either Method 3010 or Method 3050. There is no hard digestion for Sb at this time.

7.2 See Method 7000, Paragraph 7.2, Direct Aspiration Procedure.

8.0 QUALITY CONTROL

8.1 See Section 8.0 of Method 7000.

9.0 METHOD PERFORMANCE

9.1 The performance characteristics for an aqueous sample free of interferences are:

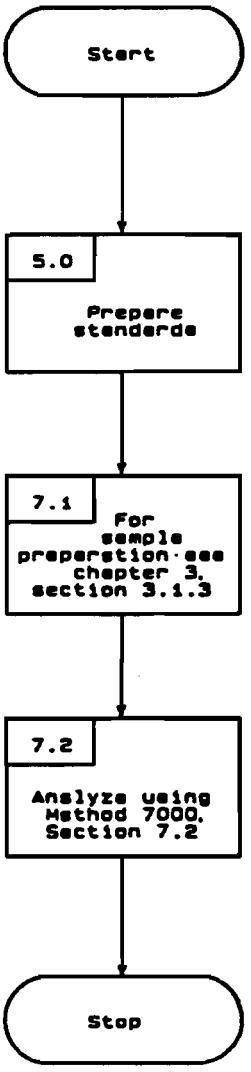
Optimum concentration range: 1-40 mg/L with a wavelength of 217.6 nm.
Sensitivity: 0.5 mg/L.
Detection limit: 0.2 mg/L.

9.2 In a single laboratory, analysis of a mixed industrial-domestic waste effluent, digested with Method 3010, at concentrations of 5.0 and 15 mg Sb/L gave the standard deviations of $\pm$0.08 and $\pm$0.1, respectively. Recoveries at these levels were 96% and 97%, respectively.

9.3 For concentrations of antimony below 0.35 mg/L, the furnace procedure (Method 7041) is recommended.

10.0 REFERENCES

1. Methods for Chemical Analysis of Water and Wastes, EPA-600/4-82-055, December 1982, Method 204.1.


Start
5.0
Prepare standards
7.1
For sample preparation see chapter 3, section 3.1.3
7.2
Analyze using Method 7000, Section 7.2
Stop

METHOD 7041

ANTIMONY (ATOMIC ABSORPTION, FURNACE TECHNIQUE)

1.0 SCOPE AND APPLICATION

1.1 See Section 1.0 of Method 7000.

2.0 SUMMARY OF METHOD

2.1 See Section 2.0 of Method 7000.

3.0 INTERFERENCES

3.1 See Section 3.0 of Method 7000 if interferences are suspected.

3.2 High lead concentration may cause a measurable spectral interference on the 217.6-nm line. If this interference is expected, the secondary wavelength should be employed or Zeeman background correction used.

4.0 APPARATUS AND MATERIALS

4.1 For basic apparatus, see Section 4.0 of Method 7000.

4.2 Instrument parameters (general):

4.2.1 Drying time and temp: 30 sec at 125°C.
4.2.2 Ashing time and temp: 30 sec at 800°C.
4.2.3 Atomizing time and temp: 10 sec at 2700°C.
4.2.4 Purge gas: Argon or nitrogen.
4.2.5 Wavelength: 217.6 nm (primary); 231.1 nm (alternate).
4.2.6 Background correction: Required.
4.2.7 Other operating parameters should be set as specified by the particular instrument manufacturer.

NOTE: The above concentration values and instrument conditions are for a Perkin-Elmer HGA-2100, based on the use of a 20-uL injection, continuous-flow purge gas, and nonpyrolytic graphite. Smaller sizes of furnace devices or those employing faster rates of atomization can be operated using lower atomization temperatures for shorter time periods than the above-recommended settings.

5.0 REAGENTS

5.1 See Section 5.0 of Method 7000.

5.2 Preparation of standards:

5.2.1 **Stock solution:** Carefully weigh 2.7426 g of antimony potassium tartrate (analytical reagent grade) and dissolve in Type II water. Dilute to 1 liter with Type II water; 1 mL = 1 mg Sb (1,000 mg/L). Alternatively, procure a certified standard from a supplier and verify by comparison with a second standard.

5.2.2 Prepare dilutions of the stock solution to be used as calibration standards at the time of analysis. The calibration standards should contain 0.2% (v/v) HNO_3 and 1-2% (v/v) HCl, prepared using the same types of acid and at the same concentrations as in the sample after processing.

6.0 SAMPLE COLLECTION, PRESERVATION, AND HANDLING

6.1 See Chapter Three, Section 3.1.3, Sample Handling and Preservation.

7.0 PROCEDURE

7.1 Sample preparation: The procedures for preparation of the sample are given in Method 3005. Method 3005, a soft digestion, is presently the only digestion procedure recommended for Sb. It yields better recoveries than either Method 3010 or Method 3050. There is no hard digestion for Sb at this time.

NOTE: The addition of HCl acid to the digestate prevents the furnace analysis of this digestate for many other metals.

7.2 See Method 7000, Paragraph 7.3, Furnace Procedure. The calculation is given in Method 7000, Paragraph 7.4.

8.0 QUALITY CONTROL

8.1 See Section 8.0 of Method 7000.

9.0 METHOD PERFORMANCE

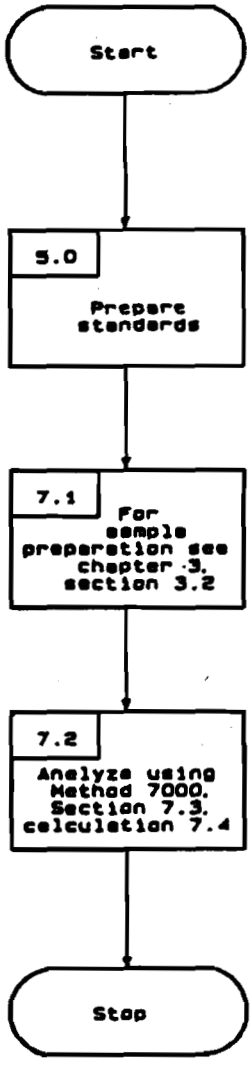
9.1 Precision and accuracy data are not available at this time.

9.2 The performance characteristics for an aqueous sample free of interferences are:

Optimum concentration range: 20-300 ug/L.
Detection limit: 3 ug/L.

10.0 REFERENCES

1. Methods for Chemical Analysis of Water and Wastes, EPA-600/4-82-055, December 1982, Method 204.2.


Start
5.0
Prepare standards
7.1
For sample preparation see chapter 3, section 3.2
7.2
Analyze using Method 7000, Section 7.3, calculation 7.4
Stop

METHOD 7060A

ARSENIC (ATOMIC ABSORPTION, FURNACE TECHNIQUE)

1.0 SCOPE AND APPLICATION

1.1 Method 7060 is an atomic absorption procedure approved for determining the concentration of arsenic in wastes, mobility procedure extracts, soils, and ground water. All samples must be subjected to an appropriate dissolution step prior to analysis.

2.0 SUMMARY OF METHOD

2.1 Prior to analysis by Method 7060, samples must be prepared in order to convert organic forms of arsenic to inorganic forms, to minimize organic interferences, and to convert the sample to a suitable solution for analysis. The sample preparation procedure varies depending on the sample matrix. Aqueous samples are subjected to the acid digestion procedure described in this method. Sludge samples are prepared using the procedure described in Method 3050.

2.2 Following the appropriate dissolution of the sample, a representative aliquot of the digestate is spiked with a nickel nitrate solution and is placed manually or by means of an automatic sampler into a graphite tube furnace. The sample aliquot is then slowly evaporated to dryness, charred (ashed), and atomized. The absorption of hollow cathode or EDL radiation during atomization will be proportional to the arsenic concentration. Other modifiers may be used in place of nickel nitrate if the analyst documents the chemical and concentration used.

2.3 The typical detection limit for water samples using this method is 1 ug/L. This detection limit may not be achievable when analyzing waste samples.

3.0 INTERFERENCES

3.1 Elemental arsenic and many of its compounds are volatile; therefore, samples may be subject to losses of arsenic during sample preparation. Spike samples and relevant standard reference materials should be processed to determine if the chosen dissolution method is appropriate.

3.2 Likewise, caution must be employed during the selection of temperature and times for the dry and char (ash) cycles. A matrix modifier such as nickel nitrate must be added to all digestates prior to analysis to minimize volatilization losses during drying and ashing.

3.3 In addition to the normal interferences experienced during graphite furnace analysis, arsenic analysis can suffer from severe nonspecific absorption and light scattering caused by matrix components during atomization. Arsenic analysis is particularly susceptible to these problems because of its low analytical wavelength (193.7 nm). Simultaneous background correction must be employed to avoid erroneously high results. Aluminum is a severe positive interferent in the analysis of arsenic, especially using D_2 arc background

correction. Although Zeeman background correction is very useful in this situation, use of any appropriate background correction technique is acceptable.

3.4 If the analyte is not completely volatilized and removed from the furnace during atomization, memory effects will occur. If this situation is detected by means of blank burns, the tube should be cleaned by operating the furnace at full power at regular intervals in the analytical scheme.

4.0 APPARATUS AND MATERIALS

4.1 Griffin beaker or equivalent: 250 mL.

4.2 Class A Volumetric flasks: 10-mL.

4.3 Atomic absorption spectrophotometer: Single or dual channel, single- or double-beam instrument having a grating monochromator, photo-multiplier detector, adjustable slits, a wavelength range of 190 to 800 nm, and provisions for simultaneous background correction and interfacing with a suitable recording device.

4.4 Arsenic hollow cathode lamp, or electrodeless discharge lamp (EDL): EDLs provide better sensitivity for arsenic analysis.

4.5 Graphite furnace: Any graphite furnace device with the appropriate temperature and timing controls.

4.6 Data systems recorder: A recorder is strongly recommended for furnace work so that there will be a permanent record and so that any problems with the analysis such as drift, incomplete atomization, losses during charring, changes in sensitivity, etc., can easily be recognized.

4.7 Pipets: Microliter with disposable tips. Sizes can range from 5 to 1,000 uL, as required.

5.0 REAGENTS

5.1 Reagent water: Water should be monitored for impurities. All references to water will refer to reagent water.

5.2 Concentrated nitric acid: Acid should be analyzed to determine levels of impurities. If a method blank using the acid is <MDL, the acid can be used.

5.3. Hydrogen peroxide (30%): Oxidant should be analyzed to determine levels of impurities. If a method blank using the H_2O_2 is <MDL, the reagent can be used.

5.4 Arsenic standard stock solution (1,000 mg/L): Either procure a certified aqueous standard from a supplier and verify by comparison with a second standard, or dissolve 1.320 g of arsenic trioxide (As_2O_3, analytical reagent grade) or equivalent in 100 mL of reagent water containing 4 g NaOH. Acidify the solution with 20 mL concentrated HNO_3 and dilute to 1 liter (1 mL = 1 mg As).

5.5 Nickel nitrate solution (5%): Dissolve 24.780 g of ACS reagent grade $Ni(NO_3)_2 \cdot 6H_2O$ or equivalent in reagent water and dilute to 100 mL.

5.6 Nickel nitrate solution (1%): Dilute 20 mL of the 5% nickel nitrate to 100 mL with reagent water.

5.7 Arsenic working standards: Prepare dilutions of the stock solution to be used as calibration standards at the time of the analysis. Withdraw appropriate aliquots of the stock solution, add concentrated HNO_3, 30% H_2O_2, and 5% nickel nitrate solution or other appropriate matrix modifier. Amounts added should be representative of the concentrations found in the samples. Dilute to 100 mL with reagent water.

6.0 SAMPLE COLLECTION, PRESERVATION, AND HANDLING

6.1 All samples must have been collected using a sampling plan that addresses the considerations discussed in Chapter Nine of this manual.

6.2 All sample containers must be prewashed with detergents, acids, and reagent water. Plastic and glass containers are both suitable.

6.3 Special containers (e.g., containers used for volatile organic analysis) may have to be used if very volatile arsenic compounds are to be analyzed.

6.4 Aqueous samples must be acidified to a pH of <2 with nitric acid and refrigerated prior to analysis.

6.5 Although waste samples do not need to be refrigerated sample handling and storage must comply with the minimum requirements established in Chapter One.

7.0 PROCEDURE

7.1 Sample preparation: Aqueous samples should be prepared in the manner described in Paragraphs 7.1.1-7.1.3. Sludge-type samples should be prepared according to Method 3050A. The applicability of a sample-preparation technique to a new matrix type must be demonstrated by analyzing spiked samples and/or relevant standard reference materials.

7.1.1 Transfer a known volume of well-mixed sample to a 250-mL Griffin beaker or equivalent; add 2 mL of 30% H_2O_2 and sufficient concentrated HNO_3 to result in an acid concentration of 1% (v/v). Heat, until digestion is complete, at 95°C or until the volume is slightly less than 50 mL.

7.1.2 Cool, transfer to a volumetric flask, and bring back to 50 mL with reagent water.

7.1.3 Pipet 5 mL of this digested solution into a 10-mL volumetric flask, add 1 mL of the 1% nickel nitrate solution or other appropriate matrix modifier, and dilute to 10 mL with reagent water. The sample is now ready for injection into the furnace.

7.2 The 193.7-nm wavelength line and a background correction system are required. Follow the manufacturer's suggestions for all other spectrophotometer parameters.

7.3 Furnace parameters suggested by the manufacturer should be employed as guidelines. Because temperature-sensing mechanisms and temperature controllers can vary between instruments or with time, the validity of the furnace parameters must be periodically confirmed by systematically altering the furnace parameters while analyzing a standard. In this manner, losses of analyte due to overly high temperature settings or losses in sensitivity due to less than optimum settings can be minimized. Similar verification of furnace parameters may be required for complex sample matrices.

7.4 Inject a measured microliter aliquot of sample into the furnace and atomize. If the concentration found is greater than the highest standard, the sample should be diluted in the same acid matrix and reanalyzed. The use of multiple injections can improve accuracy and help detect furnace pipetting errors.

8.0 QUALITY CONTROL

8.1 Refer to section 8.0 of Method 7000.

9.0 METHOD PERFORMANCE

9.1 Precision and accuracy data are available in Method 206.2 of Methods for Chemical Analysis of Water and Wastes.

9.2 The optimal concentration range for aqueous samples using this method is 5-100 ug/L. Concentration ranges for non-aqueous samples will vary with matrix type.

9.3 The data shown in Table 1 were obtained from records of state and contractor laboratories. The data are intended to show the precision of the combined sample preparation and analysis method.

10.0 REFERENCES

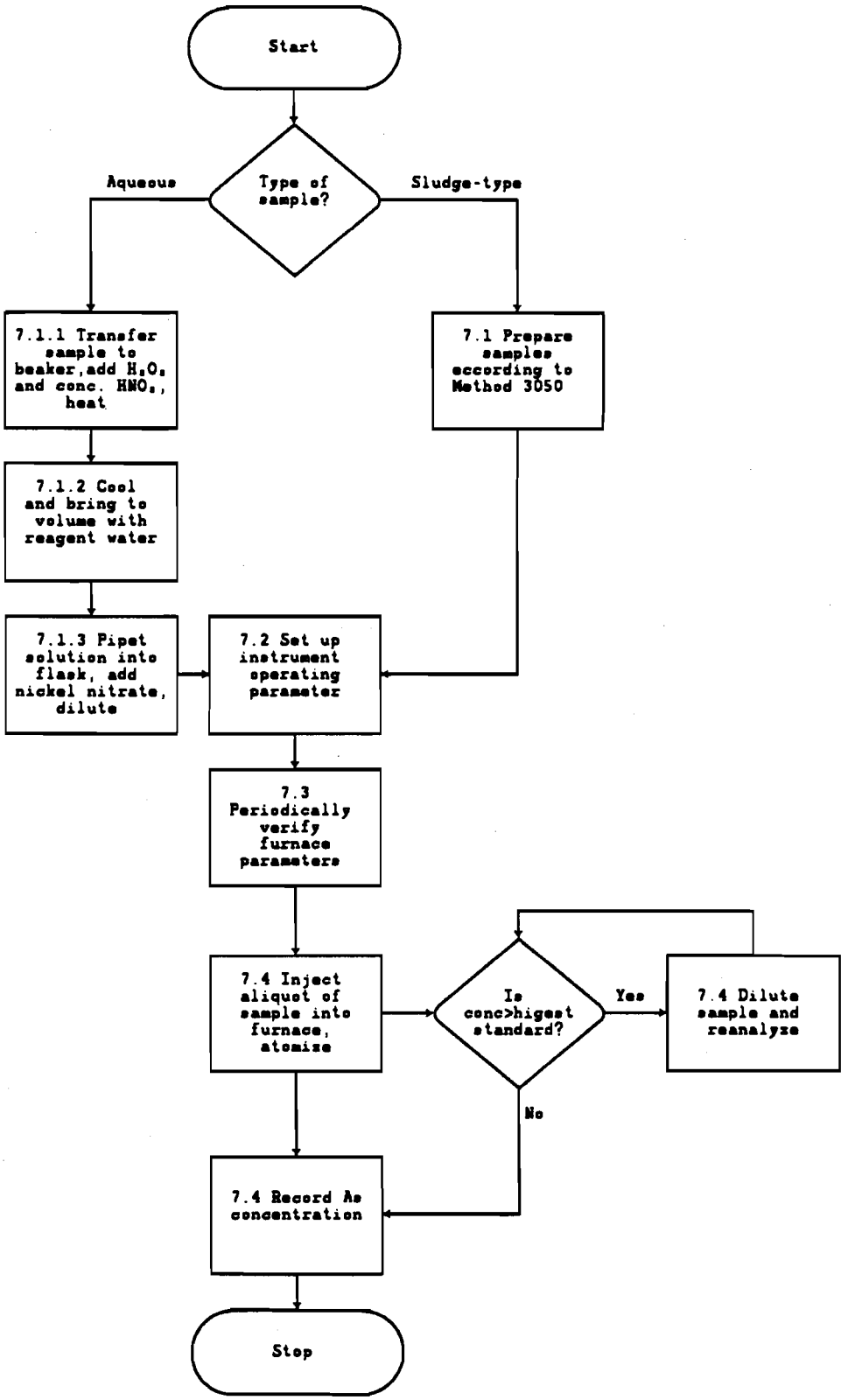
1. Methods for Chemical Analysis of Water and Wastes, EPA-600/4-82-055, December 1982, Method 206.2.

2. Gaskill, A., Compilation and Evaluation of RCRA Method Performance Data, Work Assignment No. 2, EPA Contract No. 68-01-7075, September 1986.

TABLE 1. METHOD PERFORMANCE DATA

Sample Matrix	Preparation Method	Laboratory Replicates
Contaminated soil	3050	2.0, 1.8 ug/g
Oily soil	3050	3.3, 3.8 ug/g
NBS SRM 1646 Estuarine sediment	3050	8.1, 8.33 ug/g[a]
Emission control dust	3050	430, 350 ug/g

[a]Bias of -30 and -28% from expected, respectively.


Start
Type of sample?
Aqueous
Sludge-type
7.1.1 Transfer sample to beaker, add H_2O_2 and conc. HNO_3, heat
7.1.2 Cool and bring to volume with reagent water
7.1.3 Pipet solution into flask, add nickel nitrate, dilute
7.1 Prepare samples according to Method 3050
7.2 Set up instrument operating parameter
7.3 Periodically verify furnace parameters
7.4 Inject aliquot of sample into furnace, atomize
Is conc>higest standard?
Yes
7.4 Dilute sample and reanalyze
No
7.4 Record As concentration
Stop

METHOD 7061A

ARSENIC (ATOMIC ABSORPTION, GASEOUS HYDRIDE)

1.0 SCOPE AND APPLICATION

1.1 Method 7061 is an atomic absorption procedure for determining the concentration of arsenic in wastes, mobility procedure extracts, soils, and ground water. Method 7061A is approved only for sample matrices that do not contain high concentrations of chromium, copper, mercury, nickel, silver, cobalt, and molybdenum. All samples must be subjected to an appropriate dissolution step prior to analysis. Spiked samples and relevant standard reference materials are employed to determine the applicability of the method to a given waste.

2.0 SUMMARY OF METHOD

2.1 Samples are prepared according to the nitric/sulfuric acid digestion procedure described in this method (Step 7.1). Next, the arsenic in the digestate is reduced to the trivalent form with tin chloride. The trivalent arsenic is then converted to a volatile hydride using hydrogen produced from a zinc/hydrochloric acid reaction.

2.2 The volatile hydride is swept into an argon-hydrogen flame located in the optical path of an atomic absorption spectrophotometer. The resulting absorption of the lamp radiation is proportional to the arsenic concentration.

2.3 The typical detection limit for this method is 0.002 mg/L.

3.0 INTERFERENCES

3.1 High concentrations of chromium, cobalt, copper, mercury, molybdenum, nickel, and silver can cause analytical interferences.

3.2 Traces of nitric acid left following the sample work-up can result in analytical interferences. Nitric acid must be distilled off by heating the sample until fumes of sulfur trioxide (SO_3) are observed.

3.3 Elemental arsenic and many of its compounds are volatile; therefore, certain samples may be subject to losses of arsenic during sample preparation.

4.0 APPARATUS AND MATERIALS

4.1 Beaker or equivalent - 100-mL.

4.2 Electric hot plate or equivalent - adjustable and capable of maintaining a temperature of 90-95°C.

4.3.1 Medicine dropper - Capable of fitting into a size "0" rubber stopper and delivering 1.5 mL.

4.3.2 Pear-shaped reaction flask - 50-mL, with two 14/20 necks (Scientific Glass JM-5835 or equivalent).

4.3.3 Gas inlet-outlet tube - Constructed from a micro cold-finger condenser (JM-3325) by cutting the portion below the 14/20 ground-glass joint.

4.3.4 Magnetic stirrer - To homogenize the zinc slurry.

4.3.5 Polyethylene drying tube - 10-cm, filled with glass to prevent particulate matter from entering the burner.

4.3.6 Flow meter - Capable of measuring 1 liter/min.

4.3.7 Class A volumetric flasks.

4.3.8 Graduated cylinder or equivalent.

4.4 Atomic absorption spectrophotometer - Single or dual channel, single- or double-beam instrument having a grating monochromator, photo-multiplier detector, adjustable slits, a wavelength range of 190 to 800 nm, and provisions for interfacing with a strip-chart recorder.

4.5 Burner - Recommended by the particular instrument manufacturer for the argon-hydrogen flame.

4.6 Arsenic hollow cathode lamp or arsenic electrodeless discharge lamp.

4.7 Strip-chart recorder.

5.0 REAGENTS

5.1 Reagent grade chemicals shall be used in all tests. Unless otherwise indicated, it is intended that all reagents shall conform to the specifications of the Committee on Analytical Reagents of the American Chemical Society, where such specifications are available. Other grades may be used, provided it is first ascertained that the reagent is of sufficiently high purity to permit its use without lessening the accuracy of the determination.

5.2 Reagent Water. Reagent water will be interferent free. All references to water in the method refer to reagent water unless otherwise specified.

5.3 Nitric acid (concentrated), HNO_3. Acid should be analyzed to determine levels of impurities. If a method blank is < MDL, the acid can be used.

5.4 Sulfuric acid (concentrated), H_2SO_4. Acid should be analyzed to determine levels of impurities. If a method blank is < MDL, the acid can be used.

5.5 Hydrochloric acid (concentrated), HCl. Acid should be analyzed to determine levels of impurities. If a method blank is < MDL, the acid can be used.

5.6 Diluent - Add 100 mL 18N H_2SO_4 and 400 mL concentrated HCl to 400 mL water and dilute to a final volume of 1 liter with water.

5.7 Potassium iodide solution - Dissolve 20 g KI in 100 mL water.

5.8 Stannous chloride solution - Dissolve 100 g $SnCl_2$ in 100 mL concentrated HCl.

5.9 Arsenic solutions

5.9.1 Arsenic standard solution (1,000 mg/L) - Either procure a certified aqueous standard from a supplier and verify by comparison with a second standard, or dissolve 1.320 g of arsenic trioxide As_2O_3 in 100 mL of water containing 4 g NaOH. Acidify the solution with 20 mL concentrated HNO_3 and dilute to 1 liter.

5.9.2 Intermediate arsenic solution - Pipet 1 mL stock arsenic solution into a 100-mL volumetric flask and bring to volume with water containing 1.5 mL concentrated HNO_3/liter (1 mL = 10 ug As).

5.9.3 Standard arsenic solution - Pipet 10 mL intermediate arsenic solution into a 100-mL volumetric flask and bring to volume with water containing 1.5 mL concentrated HNO_3/liter (1 mL = 1 ug As).

6.0 SAMPLE COLLECTION, PRESERVATION, AND HANDLING

6.1 All samples must have been collected using a sampling plan that addresses the considerations discussed in Chapter Nine of this manual.

6.2 All sample containers must be prewashed with detergents, acids, and water. Plastic and glass containers are both suitable.

6.3 Special containers (e.g. containers used for volatile organic analysis) may have to be used if very volatile arsenic compounds are to be analyzed.

6.4 Aqueous samples must be acidified to a pH of < 2 with nitric acid.

6.5 Nonaqueous samples shall be refrigerated, when possible, and analyzed as soon as possible.

7.0 PROCEDURE

7.1 Place a 50-mL aliquot of digested sample (or, in the case of analysis of EP extracts, 50 mL) of the material to be analyzed in a 100-mL beaker. Add 10 mL concentrated HNO_3 and 12 mL 18N H_2SO_4. Evaporate the sample in the hood on an electric hot plate until white SO_3 fumes are observed (a volume of about 20 mL). Do not let the sample char. If charring occurs, immediately turn off the heat, cool, and add an additional 3 mL of HNO_3. Continue to add additional HNO_3 in order to maintain an excess (as evidenced by the formation of brown fumes). Do not let the solution darken, because arsenic may be reduced and lost. When the sample remains colorless or straw yellow during evolution of SO_3 fumes, the digestion is complete. Cool the sample, add about 25 mL water, and again evaporate until SO_3 fumes are produced in order to expel oxides of nitrogen. Cool. Transfer the digested sample to a 100-mL volumetric flask. Add 40 mL of concentrated HCl and bring to volume with water.

7.2 Prepare working standards from the standard arsenic solution. Transfer 0, 0.5, 1.0, 1.5, 2.0, and 2.5 mL of standard to 100-mL volumetric flasks and bring to volume with diluent. These concentrations will be 0, 5, 10, 15, 20, and 25 ug As/liter.

7.3 If EP extracts are being analyzed or if a matrix interference is encountered, take the 15-, 20-, and 25-mg/liter standards and quantitatively transfer 25 mL of each of these standards into separate 50-mL volumetric flasks. Add 10 mL of the prepared sample to each flask. Bring to volume with water containing 1.5 mL HCl/liter.

7.4 Add 10 mL of prepared sample to a 50-mL volumetric flask. Bring to volume with water containing 1.5 mL HCl/liter. This is the zero addition aliquot.

NOTE: The absorbance from the zero addition aliquot will be one-fifth that produced by the prepared sample. The absorbance from the spiked samples will be one-half that produced by the standards plus the contribution from one-fifth of the prepared sample. Keeping these absorbances in mind will assist in judging the correct dilutions to produce optimum absorbance.

7.5 Transfer a 25-mL portion of the digested sample or standard to the reaction vessel and add 1 mL KI solution. Add 0.5 mL $SnCl_2$ solution. Allow at least 10 minutes for the metal to be reduced to its lowest oxidation state. Attach the reaction vessel to the special gas inlet-outlet glassware. Fill the medicine dropper with 1.50 mL zinc slurry that has been kept in suspension with the magnetic stirrer. Firmly insert the stopper containing the medicine dropper into the side neck of the reaction vessel. Squeeze the bulb to introduce the zinc slurry into the sample or standard solution. The metal hydride will produce a peak almost immediately. After the recorder pen begins to return to the base line, the reaction vessel can be removed.

CAUTION: Arsine is very toxic. Precautions must be taken to avoid inhaling arsine gas.

7.6 Use the 193.7-nm wavelength and background correction for the analysis of arsenic.

7.7 Follow the manufacturer's instructions for operating an argon-hydrogen flame. The argon-hydrogen flame is colorless; therefore, it may be useful to aspirate a low concentration of sodium to ensure that ignition has occurred.

7.8 If the method of standard additions was employed, plot the absorbances of spiked samples and blank vs. the concentrations. The extrapolated value will be one-fifth the concentration of the original sample. If the plot does not result in a straight line, a nonlinear interference is present. This problem can sometimes be overcome by dilution or addition of other reagents if there is some knowledge about the waste. If the method of standard additions was not required, then the concentration can be part of the calibration curve.

8.0 QUALITY CONTROL

8.1 Refer to section 8.0 of Method 7000.

9.0 METHOD PERFORMANCE

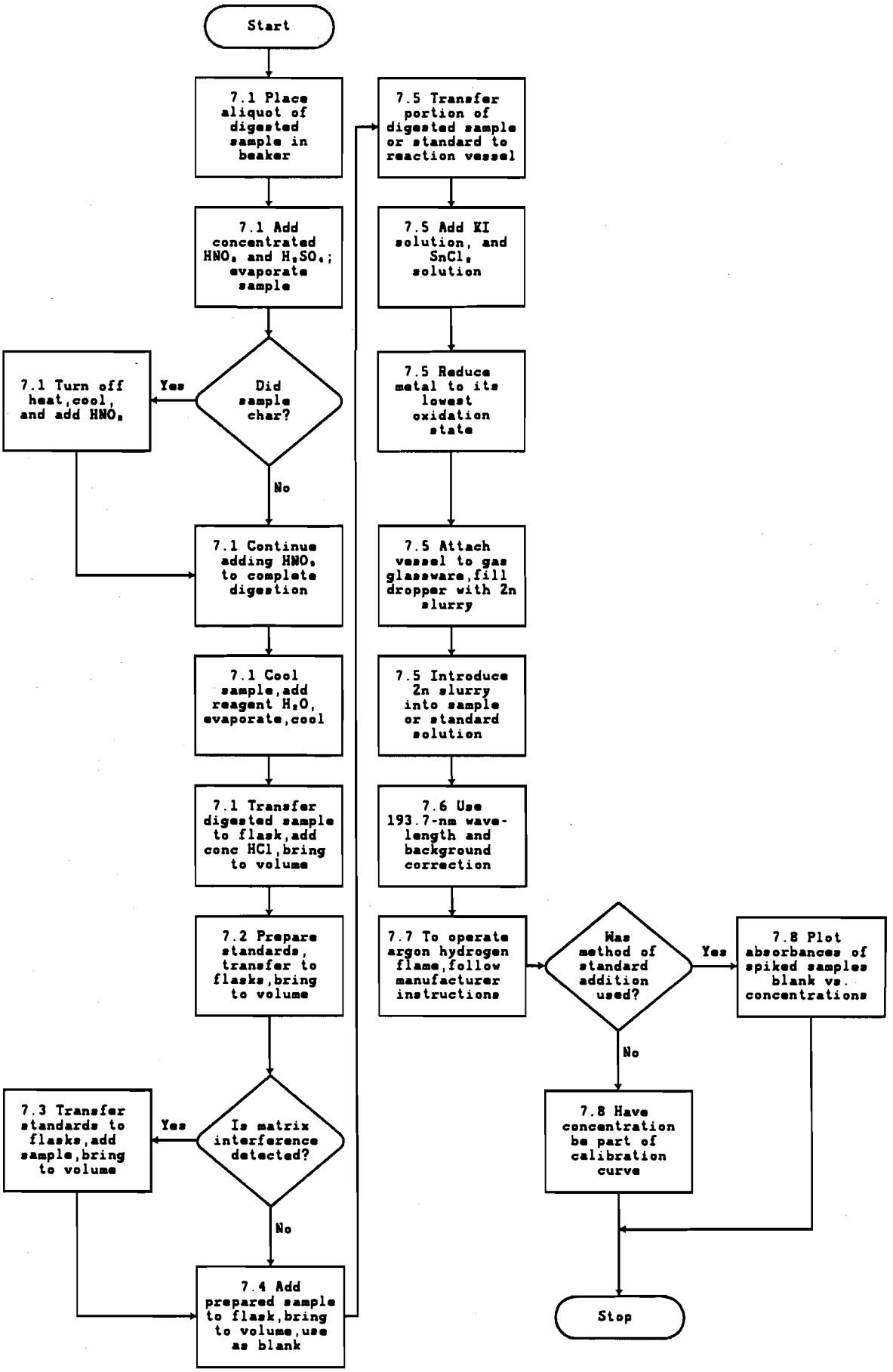
9.1 Precision and accuracy data are available in Method 206.3 of Methods for Chemical Analysis of Water and Wastes.

10.0 REFERENCES

1. Methods For Chemical Analysis of Water and Wastes, EPA-600/4-82-055, December 1982, Method 206.3.

2. Rohrbough, W.G.; et al. Reagent Chemicals, American Chemical Society Specifications, 7th ed.; American Chemical Society: Washington, DC, 1986.

3. 1985 Annual Book of ASTM Standards, Vol. 11.01; "Standard Specification for Reagent Water"; ASTM: Philadelphia, PA, 1985; D1193-77.


Start
7.1 Place aliquot of digested sample in beaker
7.1 Add concentrated HNO_3 and H_2SO_4; evaporate sample
Did sample char?
Yes
7.1 Turn off heat, cool, and add HNO_3
No
7.1 Continue adding HNO_3 to complete digestion
7.1 Cool sample, add reagent H_2O_2, evaporate, cool
7.1 Transfer digested sample to flask, add conc HCl, bring to volume
7.2 Prepare standards, transfer to flasks, bring to volume
Is matrix interference detected?
Yes
7.3 Transfer standards to flasks, add sample, bring to volume
No
7.4 Add prepared sample to flask, bring to volume, use as blank
7.5 Transfer portion of digested sample or standard to reaction vessel
7.5 Add KI solution, and $SnCl_2$ solution
7.5 Reduce metal to its lowest oxidation state
7.5 Attach vessel to gas glassware, fill dropper with Zn slurry
7.5 Introduce Zn slurry into sample or standard solution
7.6 Use 193.7-nm wavelength and background correction
7.7 To operate argon hydrogen flame, follow manufacturer instructions
Was method of standard addition used?
Yes
7.8 Plot absorbances of spiked samples blank vs. concentrations
No
7.8 Have concentration be part of calibration curve
Stop

METHOD 7062

ANTIMONY AND ARSENIC (ATOMIC ABSORPTION, BOROHYDRIDE REDUCTION)

1.0 SCOPE AND APPLICATION

1.1 Method 7062 is an atomic absorption procedure for determining 1 µg/L to 400 µg/L concentrations of antimony and arsenic in wastes, mobility procedure extracts, soils, and ground water. Method 7062 is approved for sample matrices that contain up to a total of 4000 mg/L concentrations of cobalt, copper, iron, mercury, or nickel. A solid sample can contain up to 40% by weight of the interferents before exceeding 4000 mg/L in a digested sample. All samples including aqueous matrices must be subjected to an appropriate dissolution step prior to analysis. Spiked samples and relevant standard reference materials are used to determine the applicability of the method to a given waste.

2.0 SUMMARY OF METHOD

2.1 Samples are prepared according to the nitric acid digestion procedure described in Method 3010 for aqueous and extract samples and the nitric/peroxide/hydrochloric acid digestion procedure described in Method 3050 (furnace AA option) for sediments, soils, and sludges. Excess peroxide is removed by evaporating samples to near dryness at the end of the digestion followed by degassing the samples upon addition of urea. L-cysteine is then added as a masking agent. Next, the antimony and arsenic in the digest are reduced to the trivalent forms with potassium iodide. The trivalent antimony and arsenic are then converted to volatile hydrides using hydrogen produced from the reaction of the acidified sample with sodium borohydride in a continuous-flow hydride generator.

2.2 The volatile hydrides are swept into, and decompose in, a heated quartz cell located in the optical path of an atomic absorption spectrophotometer. The resulting absorption of the lamp radiation is proportional to the arsenic or antimony concentration.

2.3 The typical detection limit for this method is 1.0 µg/L.

3.0 INTERFERENCES

3.1 Very high (>4000 mg/L) concentrations of cobalt, copper, iron, mercury, and nickel can cause analytical interferences through precipitation as reduced metals and associated blockage of transfer lines and fittings.

3.2 Traces of peroxides left following the sample work-up can result in analytical interferences. Peroxides must be removed by evaporating each sample to near dryness followed by reaction with urea and allowing sufficient time for degassing before analysis (see Sections 7.1 and 7.2).

3.3 Even after acid digestion, organic compounds will remain in the sample. These flame gases and these organic compounds can absorb at the analytical wavelengths and background correction must be used.

4.0 APPARATUS AND MATERIALS

4.1 Electric hot plate: Large enough to hold at least several 100 mL Pyrex digestion beakers.

4.2 A continuous-flow hydride generator: A commercially available continuous-flow sodium borohydride/HCl hydride generator or a generator constructed similarly to that shown in Figure 1 (P. S. Analytical or equivalent).

4.2.1 Peristaltic Pump: A four-channel, variable-speed peristaltic pump to permit regulation of liquid-stream flow rates (Ismatec Reglo-100 or equivalent). Pump speed and tubing diameters should be adjusted to provide the following flow rates: sample/blank flow = 4.2 mL/min; borohydride flow = 2.1 mL/min; and potassium iodide flow = 0.5 mL/min.

4.2.2 Sampling Valve (optional): A sampling valve (found in the P. S. Analytical Hydride Generation System or equivalent) that allows switching between samples and blanks (rinse solution) without introduction of air into the system will provide more signal stability.

4.2.3 Transfer Tubing and Connectors: Transfer tubing (1 mm I.D.), mixing T's, and connectors are made of a fluorocarbon (PFA or TFM) and are of compatible sizes to form tight, leak-proof connections (Latchat, Technicon, etc. flow injection apparatus accessories or equivalent).

4.2.4 Mixing Coil: A 20-turn coil made by wrapping transfer tubing around a 1-cm diameter by 5-cm long plastic or glass rod (see Figure 1).

4.2.5 Mixing Coil Heater, if appropriate: A 250-mL Erlenmeyer flask containing 100 mL of water heated to boiling on a dedicated one-beaker hotplate (Corning PC-35 or equivalent). The mixing coil in 4.2.4 is immersed in the boiling water to speed kinetics of the hydride forming reactions and increase solubility of interfering reduced metal precipitates.

4.2.6 Gas-Liquid Separator: A glass apparatus for collecting and separating liquid and gaseous products (P.T. Analytical accessory or equivalent) which allows the liquid fraction to drain to waste and gaseous products above the liquid to be swept by a regulated carrier gas (argon) out of the cell for analysis. To avoid undue carrier gas dilution, the gas volume above the liquid should not exceed 20 mL. See Figure 1 for an acceptable separator shape.

4.2.7 Condensor: Moisture picked up by the carrier gas must be removed before encountering the hot absorbance cell. The moist carrier gas with the hydrides is dried by passing the gasses through a small (< 25

mL) volume condensor coil (Ace Glass Model 6020-02 or equivalent) that is cooled to 5°C by a water chiller (Neslab RTE-110 or equivalent). Cool tap-water in place of a chiller is acceptable.

4.2.8 Flow Meter/Regulator: A meter capable of regulating up to 1 L/min of argon carrier gas is recommended.

4.3 Absorbance Cell: A 17 cm or longer quartz tube T-cell (windowless is strongly suggested) is recommended, as shown in Figure 1 (Varian Model VGA-76 accessory or equivalent). The cell is held in place by a holder that positions the cell about 1 cm over a conventional AA air-acetylene burner head. In operation, the cell is heated to around 900°C.

4.4 Atomic absorption spectrophotometer: Single or dual channel, single- or double-beam instrument having a grating monochromator, photomultiplier detector, adjustable slits, a wavelength range of 190 to 800 nm, and provisions for interfacing with an appropriate recording device.

4.5 Burner: As recommended by the particular instrument manufacturer for an air-acetylene flame. An appropriate mounting bracket attached to the burner that suspends the quartz absorbance cell between 1 and 2 cm above the burner slot is required.

4.6 Antimony and arsenic hollow cathode lamps or antimony and arsenic electrodeless discharge lamps and power supply. Super-charged hollow-cathode lamps or EDL lamps are recommended for maximum sensitivity.

4.7 Strip-chart recorder (optional): Connect to output of spectrophotometer.

5.0 REAGENTS

5.1 Reagent water: Water must be monitored for impurities. Refer to Chapter 1 for definition of Reagent water.

5.2 Concentrated nitric acid (HNO_3): Acid must be analyzed to determine levels of impurities. If a method blank is <MDL, the acid can be used.

5.3 30% Hydrogen peroxide (H_2O_2): Peroxide must be a tin-free grade.

5.4 Concentrated hydrochloric acid (HCl): Acid must be analyzed to determine levels of impurities. If a method blank is <MDL, the acid can be used.

5.5 Diluent solution: A 3% HCl solution in reagent water must be prepared as a diluent solution if excessive levels of analytes or interfering metals are found in the undiluted samples.

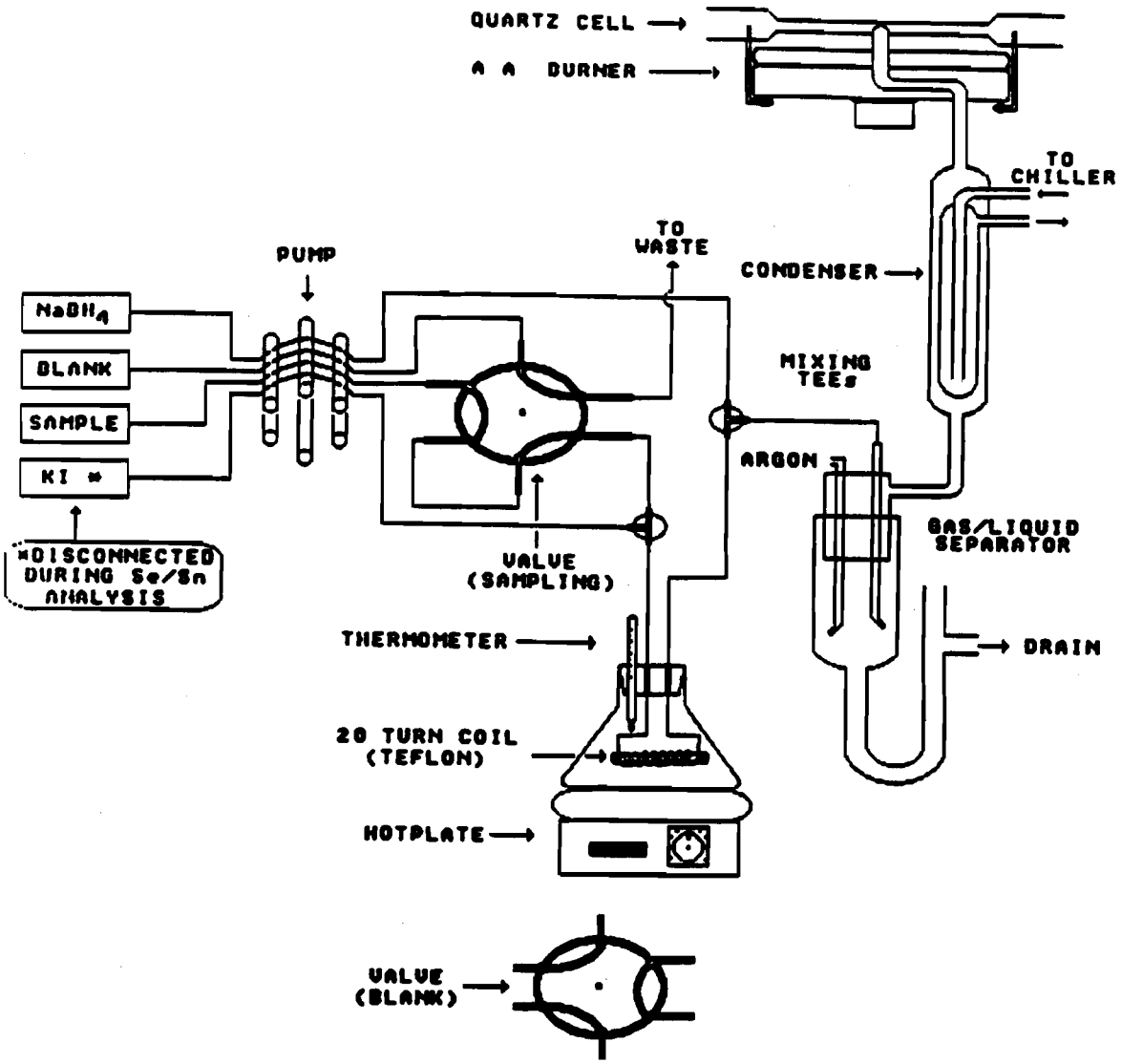


Figure 1. Continuous-flow sodium borohydride/hydride generator apparatus set-up and an AAS sample introduction system.

5.6 Urea (H_2NCONH_2): A 5.00-g portion of reagent grade urea must be added to a 25-mL aliquot of each sample for removal of excess peroxide through degassing (see Section 7.2).

5.7 L-cysteine ($C_6H_{12}N_2O_4S_2$): A 1.00-g portion of reagent grade L-cystine must be added to a 25-mL aliquot of each sample for masking the effects of suppressing transition metals (see Section 7.2).

5.8 20% Potassium iodide (KI): A 20% KI solution (20 g reagent-grade KI dissolved and brought to volume in 100 mL reagent water) must be prepared for reduction of antimony and arsenic to their +3 valence states.

5.9 4% Sodium borohydride ($NaBH_4$): A 4% sodium borohydride solution (20 g reagent-grade $NaBH_4$ plus 2 g sodium hydroxide dissolved in 500 mL of reagent water) must be prepared for conversion of the antimony and arsenic to their hydrides.

5.10 Analyte solutions:

5.10.1 **Antimony and arsenic stock standard solution** (1,000 mg/L): Either procure certified aqueous standards from a supplier and verify by comparison with a second standard, or dissolve 1.197 g of antimony trioxide Sb_2O_3 and 1.320 g of arsenic trioxide As_2O_3 in 100 mL of reagent water containing 4 g NaOH. Acidify the solution with 20 mL concentrated HNO_3 and dilute to 1 liter.

5.10.2 **Intermediate antimony and arsenic solution:** Pipet 1 mL stock antimony and arsenic solution into a 100-mL volumetric flask and bring to volume with reagent water containing 1.5 mL concentrated HNO_3/liter (1 mL = 10 μg each of Sb and As).

5.10.3 **Standard antimony and arsenic solution:** Pipet 10 mL intermediate antimony and arsenic solution into a 100-mL volumetric flask and bring to volume with reagent water containing 1.5 mL concentrated HNO_3/liter (1 mL = 1 μg each of Sb and As).

6.0 SAMPLE COLLECTION, PRESERVATION, AND HANDLING

6.1 All samples must have been collected using a sampling plan that addresses the considerations discussed in Chapter Nine of this manual.

6.2 All sample containers must be prewashed with detergents, acids, and reagent water. Plastic and glass containers are both suitable.

6.3 Special containers (e.g., containers used for volatile organic analysis) may have to be used if very volatile antimony and arsenic compounds are suspected to be present in the samples.

6.4 Aqueous samples must be acidified to a pH of <2 with nitric acid.

6.5 Nonaqueous samples shall be refrigerated, when possible, and analyzed as soon as possible.

7.0 PROCEDURE

7.1 Place a 100-mL portion of an aqueous sample or extract or 1.000 g of a dried solid sample in a 250-mL digestion beaker. Digest aqueous samples and extracts according to Method 3010. Digest solid samples according to Method 3050 (furnace AA option) with the following modifications: add 5 mL of concentrated hydrochloric acid just prior to the final volume reduction stage to aid in antimony recovery; the final volume reduction should be to less than 5 mL but not to dryness to adequately remove excess hydrogen peroxide (see note). After dilution to volume, further dilution with diluent may be necessary if analytes are known to exceed 400 µg/L or if interferents are expected to exceed 4000 mg/L in the digestate.

> Note: For solid digestions, the volume reduction stage is critical to obtain accurate data, especially for arsenic. Close monitoring of each sample is necessary when this critical stage is reached.

7.2 Prepare samples for hydride analysis by adding 5.00 g urea, 1.00 g L-cysteine, and 20 mL concentrated HCl to a 25-mL aliquot of digested sample in a 50-mL volumetric flask. Heat in a water bath until the L-cysteine has dissolved and effervescence has subsided (At least 30 minutes is suggested. If effervescense is still seen, repeat step 7.1 with more volume reduction.). Bring flask to volume with reagent water before analyzing. A 1:1 dilution correction must be made in the final concentration calculations.

7.3 Prepare working standards from the standard antimony and arsenic solution. Transfer 0, 0.5, 1.0, 1.5, 2.0, and 2.5 mL of standard to 100-mL volumetric flasks and bring to volume with diluent. These concentrations will be 0, 5, 10, 15, 20, and 25 µg Sb and As/liter.

7.4 If EP extracts (Method 1310) are being analyzed for arsenic, the method of standard additions must be used. Spike appropriate amounts of intermediate or standard antimony and arsenic solution to three 25 mL aliquots of each unknown. Spiking volumes should be kept less than 0.250 mL to avoid excessive spiking dilution errors.

7.5 Set up instrumentation and hydride generation apparatus and fill reagent containers. The sample and blank flows should be set around 4.2 mL/min, the borohydride flow around 2.1 mL/min, and the potassium iodide flow around 0.5 mL/min. The argon carrier gas flow is adjusted to about 200 mL/min. For the AA, use the 217.6-nm wavelength and 0.7-nm slit width (or manufacturer's recommended slit-width) without background correction if analyzing for antimony. Use the 193.7-nm wavelength and 0.7-nm slit width (or manufacturer's recommended slit-width) with background correction for the analysis of arsenic. Begin all flows and allow 10 minutes for warm-up.

7.6 Place sample feed line into a prepared sample solution and start pump to begin hydride generation. Wait for a maximum steady-state signal on the strip-chart recorder or output meter. Switch to blank sample and watch for signal to decline to baseline before switching to the next sample and beginning the next analysis. Run standards first (low to high), then unknowns. Include appropriate QA/QC solutions, as required. Prepare calibration curves and convert absorbances to concentration. If a heating coil is not being used, KI must be added to the samples and heated for thirty minutes to ensure reduction.

CAUTION: The hydrides of antimony and arsenic are very toxic. Precautions must be taken to avoid inhaling the gas.

7.7 If the method of standard additions was employed, plot the measured concentration of the spiked samples and unspiked sample versus the spiked concentrations. The spiked concentration axis intercept will be the method of standard additions concentration. If the plot does not result in a straight line, a nonlinear interference is present. This problem can sometimes be overcome by dilution or addition of other reagents if there is some knowledge about the waste. If the method of standard additions was not required, then the concentration is determined from a standard calibration curve.

8.0 QUALITY CONTROL

8.1 See section 8.0 of Method 7000.

9.0 METHOD PERFORMANCE

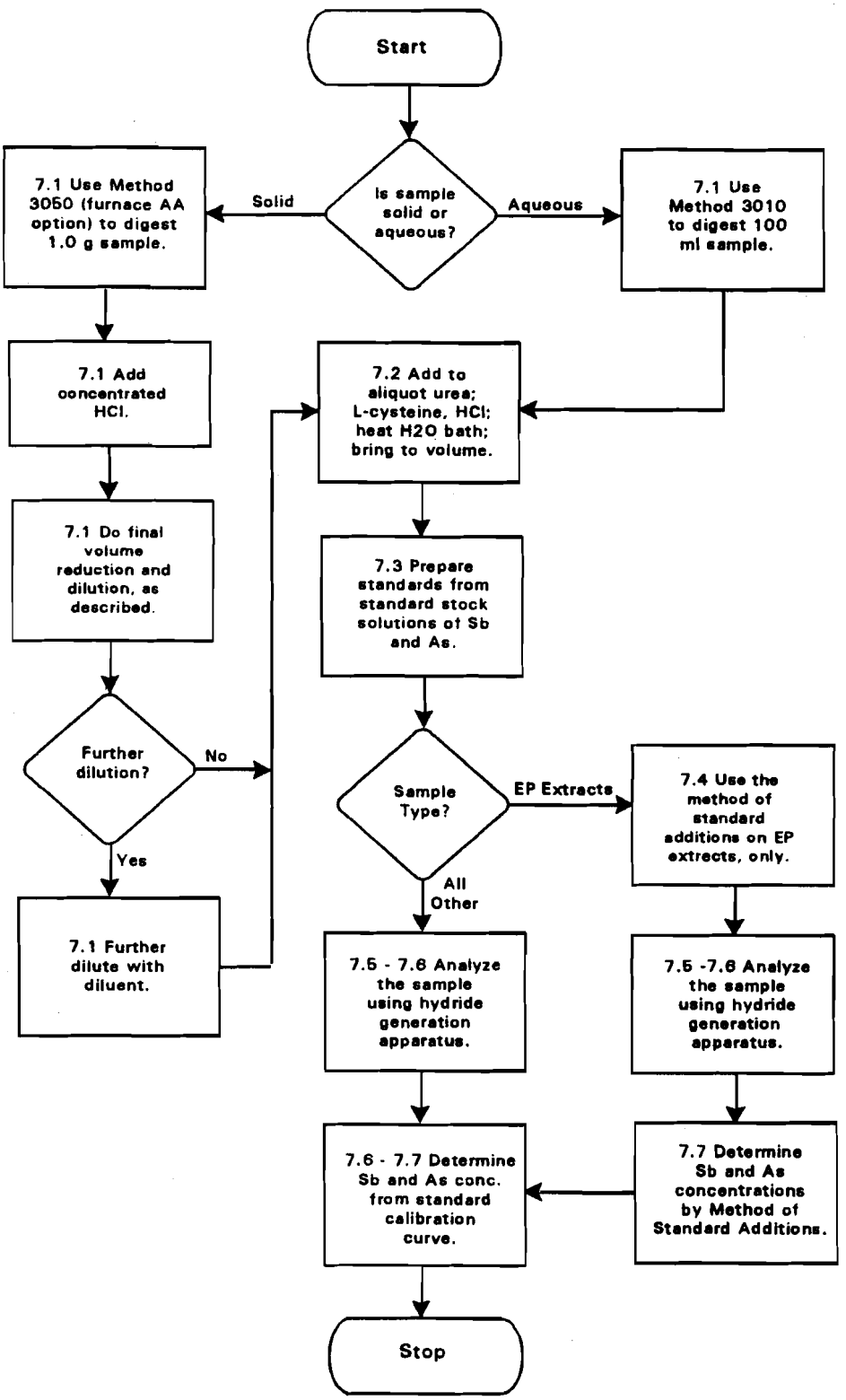
9.1 The relative standard deviations obtained by a single laboratory for 7 replicates of a contaminated soil were 18% for antimony at 9.1 ug/L in solution and 4.6% for arsenic at 68 ug/L in solution. The average percent recovery of the analysis of an 8 μg/L spike on ten different samples is 103.7% for arsenic and 95.6% for antimony.

10.0 REFERENCES

1. Methods for Chemical Analysis of Water and Wastes, EPA-600/4-82-055, December 1982, Method 206.3.

2. "Evaluation of Hydride Atomic Absorption Methods for Antimony, Arsenic, Selenium, and Tin", an EMSL-LV internal report under Contract 68-03-3249, Job Order 70.16, prepared for T. A. Hinners by D. E. Dobb, and J. D. Lindner of Lockheed Engineering and Sciences Co., and L. V. Beach of the Varian Corporation.

METHOD 7062
ANTIMONY AND ARSENIC (ATOMIC ABSORPTION, BOROHYDRIDE REDUCTION)



METHOD 7080A

BARIUM (ATOMIC ABSORPTION, DIRECT ASPIRATION)

1.0 SCOPE AND APPLICATION

1.1 See Section 1.0 of Method 7000.

2.0 SUMMARY OF METHOD

2.1 See Section 2.0 of Method 7000.

3.0 INTERFERENCES

3.1 See Section 3.0 of Method 7000 if interferences are suspected.

3.2 High hollow cathode current settings and a narrow spectral band pass must be used, because both barium and calcium emit strongly at barium's analytical wavelength.

3.3 Barium undergoes significant ionization in the nitrous oxide/acetylene flame, resulting in a significant decrease in sensitivity. All samples and standards must contain a ionization suppressant. The type of suppressant and concentration used must be documented.

4.0 APPARATUS AND MATERIALS

4.1 For basic apparatus, see Section 4.0 of Method 7000.

4.2 Instrument parameters (general):

4.2.1 Barium hollow cathode lamp.
4.2.2 Wavelength: 553.6 nm.
4.2.3 Fuel: Acetylene.
4.2.4 Oxidant: Nitrous oxide.
4.2.5 Type of flame: Fuel rich.
4.2.6 Background correction: Not required.

5.0 REAGENTS

5.1 See Section 5.0 of Method 7000.

5.2 Preparation of standards:

5.2.1 Stock solution: Dissolve 1.7787 g barium chloride ($BaCl_2 \cdot 2H_2O$) analytical reagent grade in reagent water and dilute to 1 liter (1000 mg/L). Alternatively, procure a certified standard from a supplier and verify by comparison with a second standard.

5.2.2 Prepare dilutions of the stock solution to be used as calibration standards at the time of analysis. The calibration standards

should be prepared using the same type of acid and at the same concentration as will result in the sample to be analyzed after processing. All calibration standards and samples should contain the ionization suppressant.

6.0 SAMPLE COLLECTION, PRESERVATION, AND HANDLING

6.1 See Chapter Three, Section 3.1.3, Sample Handling and Preservation.

7.0 PROCEDURE

7.1 Sample preparation: The procedures for preparation of the sample are given in Chapter Three, Section 3.2.

7.2 See Method 7000, Section 7.2, Direct Aspiration.

8.0 QUALITY CONTROL

8.1 See Section 8.0 of Method 7000.

9.0 METHOD PERFORMANCE

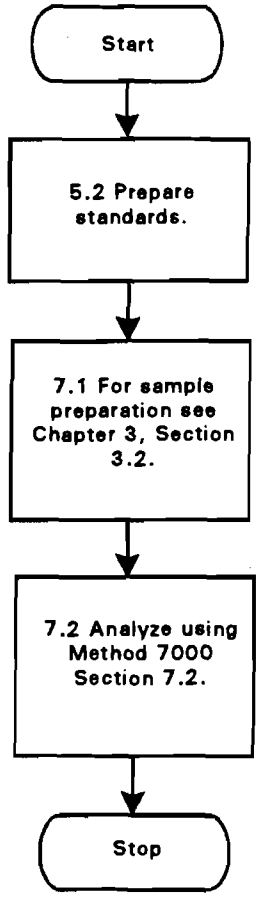
9.1 The performance characteristics for an aqueous sample free of interferences are:

Optimum concentration range: 1-20 mg/L with a wavelength of 553.6 nm.
Sensitivity: 0.4 mg/L.
Detection limit: 0.1 mg/L.

9.2 In a single laboratory, analysis of a mixed industrial-domestic waste effluent, digested with Method 3010, at concentrations of 0.4 and 2 mg Ba/L gave standard deviations of $\pm$0.043 and $\pm$0.13, respectively. Recoveries at these levels were 94% and 113%, respectively.

10.0 REFERENCES

1. Methods for Chemical Analysis of Water and Wastes, EPA-600/4-82-055, December 1982, Method 208.1.


Start
5.2 Prepare standards.
7.1 For sample preparation see Chapter 3, Section 3.2.
7.2 Analyze using Method 7000 Section 7.2.
Stop

METHOD 7081

BARIUM (ATOMIC ABSORPTION, FURNACE TECHNIQUE)

1.0 SCOPE AND APPLICATION

1.1 See Section 1.0 of Method 7000.

2.0 SUMMARY OF METHOD

2.1 See Section 2.0 of Method 7000.

3.0 INTERFERENCES

3.1 See Section 3.0 of Method 7000.

3.2 Barium is known to form a barium carbide in the graphite furnace. This less volatile carbide can cause losses of sensitivity and memory effects.

3.3 The long residence time and the high concentration of the analyte in the optical path of the graphite furnace can lead to severe physical and chemical interferences. Furnace parameters must be optimized to minimize these effects.

3.4 Because of possible chemical interaction, nitrogen should not be used as a purge gas.

3.5 Halide acids should not be used.

4.0 APPARATUS AND MATERIALS

4.1 For basic apparatus, see Section 4.0 of Method 7000.

4.2 Instrument parameters (general):

4.2.1 Drying time and temp: 30 sec at 125°C.

4.2.2 Ashing time and temp: 30 sec at 1200°C.

4.2.3 Atomizing time and temp: 10 sec at 2800°C.

4.2.4 Purge gas: Argon (nitrogen should <u>not</u> be used).

4.2.5 Wavelength: 553.6 nm.

4.2.6 Background correction: Not required.

4.2.7 Other operating parameters should be set as specified by the particular instrument manufacturer.

NOTE: The above concentration values and instrument conditions are for a Perkin-Elmer HGA-2100, based on the use of a 20-uL injection, continuous-flow purge gas, and nonpyrolytic graphite. Smaller size furnace devices or those employing faster rates of atomization can be operated using lower atomization temperatures for shorter time periods than the above-recommended settings.

5.0 REAGENTS

5.1 See Section 5.0 of Method 7000.

5.2 Preparation of standards

5.2.1 Stock solution - Dissolve 1.7787 g barium chloride ($BaCl_2$ $2H_2O$, analytical reagent grade) in water and dilute to 1 liter. Alternatively, procure a certified standard from a supplier and verify by comparison with a second standard.

5.2.2 Prepare dilutions of the stock solution to be used as calibration standards at the time of analysis. The calibration standards should be prepared using the same type of acid and at the same concentrations as in the sample after processing (0.5% v/v HNO_3).

6.0 SAMPLE COLLECTION, PRESERVATION, AND HANDLING

6.1 See Chapter Three, Step 3.1.3, Sample Handling and Preservation.

7.0 PROCEDURE

7.1 Sample Preparation - The procedures for preparation of the sample are given in Chapter Three, Step 3.2.

7.2 See Method 7000, Step 7.3, Furnace Technique.

8.0 QUALITY ASSURANCE

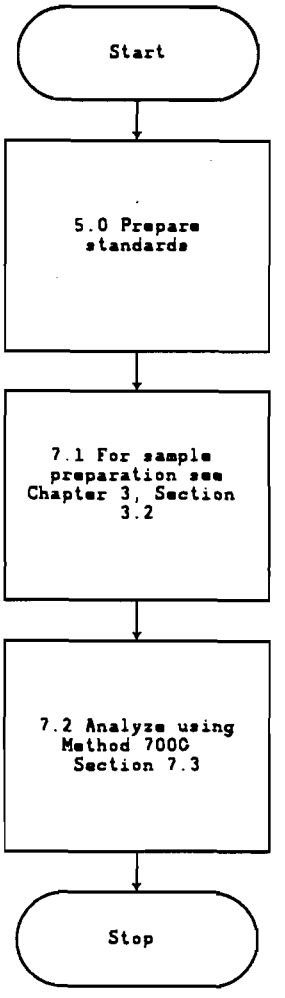
8.1 See Section 8.0 of Method 7000.

9.0 METHOD PERFORMANCE

9.1 Precision and accuracy data are not available at this time.

10.0 REFERENCES

1. Methods for Chemical Analysis of Water and Wastes; U.S. Environmental Protection Agency. Office of Research and Development. Environmental Monitoring and Support Laboratory. ORD Publication Offices of Center for Environmental Research Information: Cincinnati, OH, 1983; EPA-600/4-79-020.


Start
5.0 Prepare standards
7.1 For sample preparation see Chapter 3, Section 3.2
7.2 Analyze using Method 7000 Section 7.3
Stop

METHOD 7090

BERYLLIUM (ATOMIC ABSORPTION, DIRECT ASPIRATION)

1.0 SCOPE AND APPLICATION

1.1 See Section 1.0 of Method 7000.

2.0 SUMMARY OF METHOD

2.1 See Section 2.0 of Method 7000.

3.0 INTERFERENCES

3.1 See Section 3.0 of Method 7000 if interferences are suspected.

3.2 Background correction may be required because nonspecific absorption and light scattering can be significant at the analytical wavelength.

3.3 Concentrations of aluminum greater than 500 ppm may suppress beryllium absorbance. The addition of 0.1% fluoride has been found effective in eliminating this interference. High concentrations of magnesium and silicon cause similar problems and require the use of the method of standard additions.

4.0 APPARATUS AND MATERIALS

4.1 For basic apparatus, see Section 4.0 of Method 7000.

4.2 Instrument parameters (general):

4.2.1 **Beryllium hollow cathode lamp.**
4.2.2 **Wavelength:** 234.9 nm.
4.2.3 **Fuel:** Acetylene.
4.2.4 **Oxidant:** Nitrous oxide.
4.2.5 **Type of flame:** Fuel rich.
4.2.6 **Background correction:** Required.

5.0 REAGENTS

5.1 See Section 5.0 of Method 7000.

5.2 Preparation of standards:

5.2.1 **Stock solution:** Dissolve 11.6586 g beryllium sulfate, $BeSO_4$, in Type II water containing 2 mL nitric acid and dilute to 1 liter.

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Beryllium metal can also be dissolved in H_2SO_4. Alternatively, procure a certified standard from a supplier and verify by comparison with a second standard.

5.2.2 Prepare dilutions of the stock solution to be used as calibration standards at the time of analysis. The calibration standards should be prepared using the same type of acid and at the same concentration as will result in the sample to be analyzed after processing (0.5% v/v HNO_3).

6.0 SAMPLE COLLECTION, PRESERVATION, AND HANDLING

6.1 See Chapter Three, Section 3.1.3, Sample Handling and Preservation.

7.0 PROCEDURE

7.1 Sample Preparation: The procedures for preparation of the sample are given in Chapter Three, Section 3.2.

7.2 See Method 7000, Paragraph 7.2, Direct Aspiration.

8.0 QUALITY CONTROL

8.1 See Section 8.0 of Method 7000.

9.0 METHOD PERFORMANCE

9.1 The performance characteristics for an aqueous sample free of interferences are:

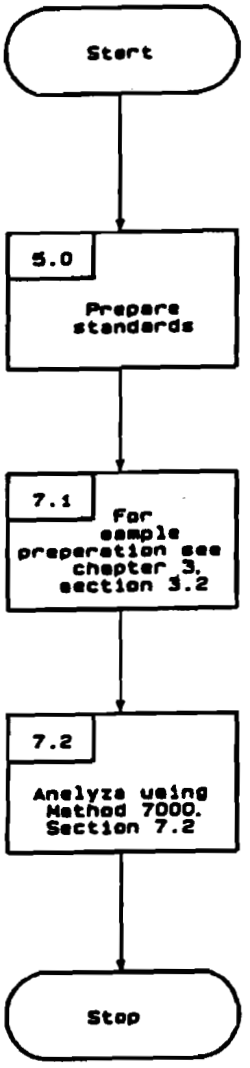
Optimum concentration range: 0.05-2 mg/L with a wavelength of 234.9 nm.
Sensitivity: 0.025 mg/L.
Detection limit: 0.005 mg/L.

9.2 In a single laboratory, analysis of a mixed industrial-domestic waste effluent, digested with Method 3010, at concentrations of 0.01 and 0.25 mg/L gave standard deviations of $\pm$0.001 and $\pm$0.002, respectively. Recoveries at these levels were 100% and 97%, respectively.

9.3 For concentrations of beryllium below 0.02 mg/L, the furnace procedure (Method 7091) is recommended.

10.0 REFERENCES

1. Methods for Chemical Analysis of Water and Wastes, EPA-600/4-82-055, December 1982, Method 210.1.


Start
5.0
Prepare standards
7.1
For sample preperation see chapter 3, section 3.2
7.2
Analyze using Method 7000, Section 7.2
Stop

METHOD 7091

BERYLLIUM (ATOMIC ABSORPTION, FURNACE TECHNIQUE)

1.0 SCOPE AND APPLICATION

1.1 See Section 1.0 of Method 7000.

2.0 SUMMARY OF METHOD

2.1 See Section 2.0 of Method 7000.

3.0 INTERFERENCES

3.1 See Section 3.0 of Method 7000 if interferences are suspected.

3.2 The long residence time and high concentrations of the atomized sample in the optical path of the graphite furnace can result in severe physical and chemical interferences. Furnace parameters must be optimized to minimize these effects.

3.3 In addition to the normal interferences experienced during graphite furnace analysis, beryllium analysis can suffer from severe nonspecific absorption and light scattering caused by matrix components during atomization. Simultaneous background correction is required to avoid erroneously high results.

4.0 APPARATUS AND MATERIALS

4.1 For basic apparatus, see Section 4.0 of Method 7000.

4.2 Instrument parameters (general):

4.2.1 **Drying time and temp:** 30 sec at 125°C.
4.2.2 **Ashing time and temp:** 30 sec at 1000°C.
4.2.3 **Atomizing time and temp:** 10 sec at 2800°C.
4.2.4 **Purge gas:** Argon.
4.2.5 **Wavelength:** 234.9 nm.
4.2.6 **Background correction:** Required.
4.2.7 Other operating parameters should be set as specified by the particular instrument manufacturer.

NOTE: The above concentration values and instrument conditions are for a Perkin-Elmer HGA-2100, based on the use of a 20-uL injection, continuous-flow purge gas, and nonpyrolytic graphite. Smaller sizes of furnace devices or those employing faster rates of atomization can be operated using lower atomization temperatures for shorter time periods than the above-recommended settings.

5.0 REAGENTS

5.1 See Section 5.0 of Method 7000.

5.2 Preparation of standards:

5.2.1 **Stock solution:** Dissolve 11.6586 g beryllium sulfate, $BeSO_4$, in Type II water containing 2 mL concentrated nitric acid and dilute to 1 liter. Beryllium metal can also be dissolved in acid. Alternatively, procure a certified standard from a supplier and verify by comparison with a second standard.

5.2.2 Prepare dilutions of the stock solution to be used as calibration standards at the time of analysis. The calibration standards should be prepared using the same type of acid and at the same concentrations as in the sample after processing (0.5% v/v HNO_3).

6.0 SAMPLE COLLECTION, PRESERVATION, AND HANDLING

6.1 See Chapter Three, Section 3.1.3, Sample Handling and Preservation.

7.0 PROCEDURE

7.1 Sample Preparation: The procedures for preparation of the sample are given in Chapter Three, Section 3.2.

7.2 See Method 7000, Paragraph 7.3, Furnace Procedure. The calculation is given in Method 7000, Paragraph 7.4.

8.0 QUALITY CONTROL

8.1 See Section 8.0 of Method 7000.

9.0 METHOD PERFORMANCE

9.1 Precision and accuracy data are not available at this time.

9.2 The performance characteristics for an aqueous sample free of interferences are:

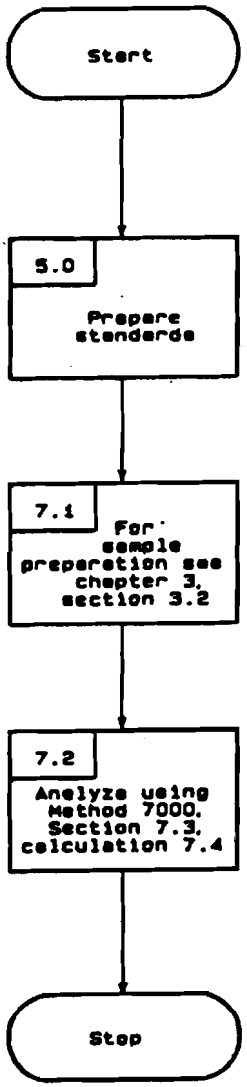
Optimum concentration range: 1-30 ug/L.
Detection limit: 0.2 ug/L.

10.0 REFERENCES

1. Methods for Chemical Analysis of Water and Wastes, EPA-600/4-82-055, December 1982, Method 210.2.

METHOD 7091

BERYLLIUM (ATOMIC ABSORPTION, FURNACE TECHNIQUE)



METHOD 7130

CADMIUM (ATOMIC ABSORPTION, DIRECT ASPIRATION)

1.0 SCOPE AND APPLICATION

1.1 See Section 1.0 of Method 7000.

2.0 SUMMARY OF METHOD

2.1 See Section 2.0 of Method 7000.

3.0 INTERFERENCES

3.1 See Section 3.0 of Method 7000 if interferences are suspected.

3.2 Nonspecific absorption and light scattering can be significant at the analytical wavelength. Thus background correction is required.

4.0 APPARATUS AND MATERIALS

4.1 For basic apparatus, see Section 4.0 of Method 7000.

4.2 Instrument parameters (general):

4.2.1 **Cadmium hollow cathode lamp.**
4.2.2 **Wavelength:** 228.8 nm.
4.2.3 **Fuel:** Acetylene.
4.2.4 **Oxidant:** Air.
4.2.5 **Type of flame:** Oxidizing (fuel lean).
4.2.6 **Background correction:** Required.

5.0 REAGENTS

5.1 See Section 5.0 of Method 7000.

5.2 Preparation of standards:

5.2.1 **Stock solution:** Dissolve 1.000 g cadmium metal (analytical reagent grade) in 20 mL of 1:1 HNO_3 and dilute to 1 liter with Type II water. Alternatively, procure a certified standard from a supplier and verify by comparison with a second standard.

5.2.2 Prepare dilutions of the stock solution to be used as calibration standards at the time of analysis. The calibration standards should be prepared using the same type of acid and at the same

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concentration as will result in the sample to be analyzed after processing.

6.0 SAMPLE COLLECTION, PRESERVATION, AND HANDLING

6.1 See Chapter Three, Section 3.1.3, Sample Handling and Preservation.

7.0 PROCEDURE

7.1 Sample preparation: The procedures for preparation of the sample are given in Chapter Three, Section 3.2.

7.2 See Method 7000, Paragraph 7.2, Direct Aspiration.

8.0 QUALITY CONTROL

8.1 See Section 8.0 of Method 7000.

9.0 METHOD PERFORMANCE

9.1 The performance characteristics for an aqueous sample free of interferences are:

Optimum concentration range: 0.05-2 mg/L with a wavelength of 228.8 nm.
Sensitivity: 0.025 mg/L.
Detection limit: 0.005 mg/L.

9.2 For concentrations of cadmium below 0.02 mg/L, the furnace procedure (Method 7131) is recommended.

9.3 Precision and accuracy data are available in Method 213.1 of Methods for Chemical Analysis of Water and Wastes.

9.4 The data shown in Table 1 were obtained from records of state and contractor laboratories. The data are intended to show the precision of the combined sample preparation and analysis method.

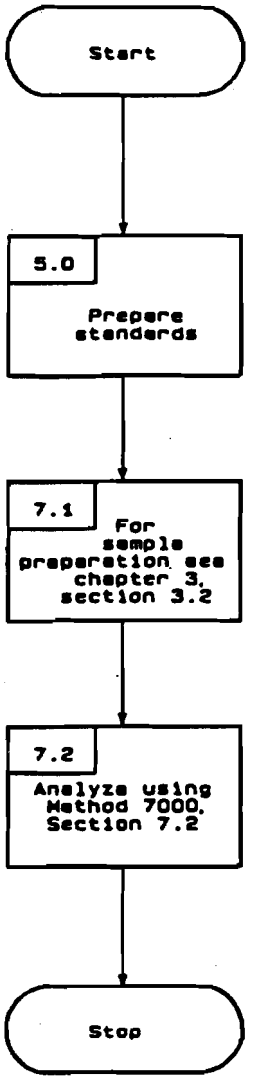
10.0 REFERENCES

1. Methods for Chemical Analysis of Water and Wastes, EPA-600/4-82-055, December 1982, Method 213.1.

2. Gaskill, A., Compilation and Evaluation of RCRA Method Performance Data, Work Assignment No. 2, EPA Contract No. 68-01-7075, September 1986.

TABLE 1. METHOD PERFORMANCE DATA

Sample Matrix	Preparation Method	Laboratory Replicates
Emission control dust	3050	2,770, 1,590 ug/g
Wastewater treatment sludge	3050	12,000, 13,000 ug/g


Start
5.0
Prepare standards
7.1
For sample preparation see chapter 3, section 3.2
7.2
Analyze using Method 7000, Section 7.2
Stop

METHOD 7131A

CADMIUM (ATOMIC ABSORPTION, FURNACE TECHNIQUE)

1.0 SCOPE AND APPLICATION

1.1 See Section 1.0 of Method 7000.

2.0 SUMMARY OF METHOD

2.1 See Section 2.0 of Method 7000.

3.0 INTERFERENCES

3.1 See Section 3.0 of Method 7000 if interferences are suspected.

3.2 In addition to the normal interferences experienced during graphite furnace analysis, cadmium analysis can suffer from severe nonspecific absorption and light scattering caused by matrix components during atomization. Simultaneous background correction is required to avoid erroneously high results.

3.3 Excess chloride may cause premature volatilization of cadmium. Ammonium phosphate used as a matrix modifier minimizes this loss. Other modifiers may be used as long as it is documented with the type of suppressant and concentration.

3.4 Many plastic pipet tips (yellow) contain cadmium. Use "cadmium-free" tips.

4.0 APPARATUS AND MATERIALS

4.1 For basic apparatus, see Section 4.0 of Method 7000.

4.2 Instrument parameters (general):

4.2.1 Drying time and temp: 30 sec at 125°C.

4.2.2 Ashing time and temp: 30 sec at 500°C.

4.2.3 Atomizing time and temp: 10 sec at 1900°C.

4.2.4 Purge gas: Argon.

4.2.5 Wavelength: 228.8 nm.

4.2.6 Background correction: Required.

4.2.7 Other operating parameters should be set as specified by the particular instrument manufacturer.

NOTE: The above concentration values and instrument conditions are for a Perkin-Elmer HGA-2100, based on the use of a 20-uL injection, continuous-flow purge gas, and nonpyrolytic graphite. Smaller sizes of furnace devices or those employing faster rates of atomization can be operated using lower atomization temperatures for shorter time periods than the above-recommended settings.

5.0 REAGENTS

5.1 See Section 5.0 of Method 7000.

5.2 Preparation of standards:

5.2.1 Stock solution: Dissolve 1.000 g of cadmium metal (analytical reagent grade) in 20 mL of 1:1 HNO_3 and dilute to 1 liter with reagent water. Alternatively, procure a certified standard from a supplier and verify by comparison with a second standard.

5.2.2 Prepare dilutions of the stock cadmium solution to be used as calibration standards at the time of analysis. To each 100 mL of standard and sample alike add 2.0 mL of the ammonium phosphate solution. The calibration standards should be prepared to contain 0.5% (v/v) HNO_3.

5.2.3 Ammonium phosphate solution (40%): Dissolve 40 g of ammonium phosphate, $(NH_4)_2HPO_4$ (analytical reagent grade), in reagent water and dilute to 100 mL.

6.0 SAMPLE COLLECTION, PRESERVATION, AND HANDLING

6.1 See Chapter Three, Section 3.1.3, Sample Handling and Preservation.

7.0 PROCEDURE

7.1 Sample preparation: The procedures for preparation of the sample are provided in Chapter Three, Section 3.2.

7.2 See Method 7000, Section 7.3, Furnace Procedure. The calculation is provided in Method 7000, Section 7.4.

8.0 QUALITY CONTROL

8.1 Refer to Section 8.0 of Method 7000 .

9.0 METHOD PERFORMANCE

9.1 Precision and accuracy data are available in Method 213.2 of Methods for Chemical Analysis of Water and Wastes.

9.2 The performance characteristics for an aqueous sample free of interferences are:

Optimum concentration range: 0.5-10 ug/L.
Detection limit: 0.1 ug/L.

9.3 The data shown in Table 1 were obtained from records of state and contractor laboratories. The data are intended to show the precision of the combined sample preparation and analysis method.

10.0 REFERENCES

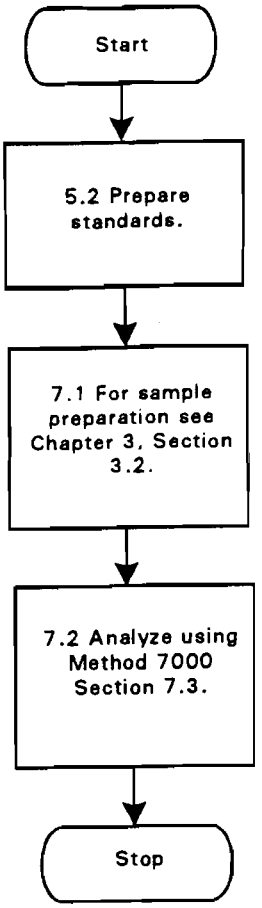
1. Methods for Chemical Analysis of Water and Wastes, EPA-600/4-82-055, December 1982, Method 213.2.

2. Gaskill, A., Compilation and Evaluation of RCRA Method Performance Data, Work Assignment No. 2, EPA Contract No. 68-01-7075, September 1986.

TABLE 1. METHOD PERFORMANCE DATA

Sample Matrix	Preparation Method	Laboratory Replicates
Lagoon soil	3050	0.10, 0.095 ug/g
NBS SRM 1646 Estuarine sediment	3050	0.35 ug/g[a]
Solvent extract of oily waste	3030	1.39, 1.09 ug/L

[a]Bias of -3% from expected value.


Start
5.2 Prepare standards.
7.1 For sample preparation see Chapter 3, Section 3.2.
7.2 Analyze using Method 7000 Section 7.3.
Stop

METHOD 7140

CALCIUM (ATOMIC ABSORPTION, DIRECT ASPIRATION)

1.0 SCOPE AND APPLICATION

1.1 See Section 1.0 of Method 7000.

2.0 SUMMARY OF METHOD

2.1 See Section 2.0 of Method 7000.

3.0 INTERFERENCES

3.1 See Section 3.0 of Method 7000.

3.2 All elements forming stable oxyanions (P, B, Si, Cr, S, V, Ti, Al, etc.) will complex calcium and interfere unless lanthanum is added. Addition of lanthanum to prepared samples rarely presents a problem because virtually all environmental samples contain sufficient calcium to require dilution to be in the linear range of the method.

3.3 PO_4, SO_4, and Al are interferents. High concentrations of Mg, Na, and K interfere.

4.0 APPARATUS AND MATERIALS

4.1 For basic apparatus, see Section 4.0 of Method 7000.

4.2 Instrument parameters (general):

4.2.1 **Calcium hollow cathode lamp.**
4.2.2 **Wavelength:** 422.7 nm.
4.2.3 **Fuel:** Acetylene.
4.2.4 **Oxidant:** Nitrous oxide.
4.2.5 **Type of flame:** Stoichiometric.
4.2.6 **Background correction:** Not required.

5.0 REAGENTS

5.1 See Section 5.0 of Method 7000.

5.2 Preparation of standards:

5.2.1 **Stock solution:** Suspend 2.500 g of $CaCO_3$ (analytical reagent grade, dried for 1 hr at 180°C) in Type II water and dissolve by adding a

minimum of dilute HCl. Dilute to 1 liter with Type II water. Alternatively, procure a certified standard from a supplier and verify by comparison with a second standard.

5.2.2 Prepare dilutions of the stock solution to be used as calibration standards at the time of analysis. The calibration standards should be prepared using the same type of acid and at the same concentration as will result in the sample to be analyzed after processing, including 1 mL of lanthanum chloride per 10 mL sample or standard (see Paragraph 5.2.3).

5.2.3 **Lanthanum chloride solution:** Dissolve 29 g La_2O_3 in 250 mL concentrated HCl -
CAUTION: REACTION IS VIOLENT -
and dilute to 500 mL with Type II water.

6.0 SAMPLE COLLECTION, PRESERVATION, AND HANDLING

6.1 See Chapter Three, Section 3.1.3, Sample Handling and Preservation.

7.0 PROCEDURE

7.1 Sample preparation: The procedures for preparation of the sample are given in Chapter Three, Section 3.2.

7.2 See Method 7000, Paragraph 7.2, Direct Aspiration.

8.0 QUALITY CONTROL

8.1 See Section 8.0 of Method 7000.

9.0 METHOD PERFORMANCE

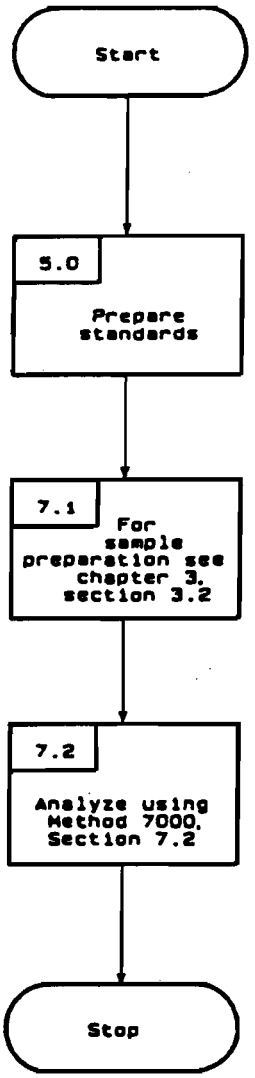
9.1 Precision and accuracy data are available in Method 215.1 of Methods for Chemical Analysis of Water and Wastes.

9.2 The performance characteristics for an aqueous sample free of interferences are:

Optimum concentration range: 0.2-7 mg/L with a wavelength of 422.7 nm.
Sensitivity: 0.08 mg/L.
Detection limit: 0.01 mg/L.

10.0 REFERENCES

1. Methods for Chemical Analysis of Water and Wastes, EPA-600/4-82-055, December 1982, Method 215.1.


Start
5.0
Prepare standards
7.1
For sample preparation see chapter 3, section 3.2
7.2
Analyze using Method 7000, Section 7.2
Stop

METHOD 7190

CHROMIUM (ATOMIC ABSORPTION, DIRECT ASPIRATION)

1.0 SCOPE AND APPLICATION

1.1 See Section 1.0 of Method 7000.

2.0 SUMMARY OF METHOD

2.1 See Section 2.0 of Method 7000.

3.0 INTERFERENCES

3.1 See Section 3.0 of Method 7000 if interferences are suspected.

3.2 An ionization interference may occur if the samples have a significantly higher alkali metal content than the standards. If this interference is encountered, an ionization suppressant (KCl) should be added to both samples and standards.

3.3 Background correction may be required because nonspecific absorption and scattering can be significant at the analytical wavelength. Background correction with certain instruments may be difficult at this wavelength due to low-intensity output from hydrogen or deuterium lamps. Consult the specific instrument manufacturer's literature for details.

4.0 APPARATUS AND MATERIALS

4.1 For basic apparatus, see Section 4.0 of Method 7000.

4.2 Instrument parameters (general):

4.2.1 **Chromium hollow cathode lamp.**
4.2.2 **Wavelength:** 357.9 nm.
4.2.3 **Fuel:** Acetylene.
4.2.4 **Oxidant:** Nitrous oxide.
4.2.5 **Type of flame:** Fuel rich.
4.2.6 **Background correction:** Not required.

5.0 REAGENTS

5.1 See Section 5.0 of Method 7000.

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5.2 Preparation of standards:

5.2.1 **Stock solution:** Dissolve 1.923 g of chromium trioxide (CrO_3, analytical reagent grade) in Type II water, acidify with redistilled HNO_3, and dilute to 1 liter. Alternatively, procure a certified standard from a supplier and verify by comparison with a second standard.

5.2.2 Prepare dilutions of the stock solution to be used as calibration standards at the time of analysis. The calibration standards should be prepared using the same type of acid and at the same concentration as will result in the sample to be analyzed after processing.

6.0 SAMPLE COLLECTION, PRESERVATION, AND HANDLING

6.1 See Chapter Three, Section 3.1.3, Sample Handling and Preservation.

7.0 PROCEDURE

7.1 Sample preparation: The procedures for preparation of the sample are given in Chapter Three, Section 3.2.

7.2 See Method 7000, Paragraph 7.2, Direct Aspiration.

8.0 QUALITY CONTROL

8.1 See Section 8.0 of Method 7000.

9.0 METHOD PERFORMANCE

9.1 The performance characteristics for an aqueous sample free of interferences are:

Optimum concentration range: 0.5-10 mg/L with a wavelength of 357.9 nm.
Sensitivity: 0.25 mg/L.
Detection limit: 0.05 mg/L.

9.2 For concentrations of chromium below 0.2 mg/L, the furnace procedure (Method 7191) is recommended.

9.3 Precision and accuracy data are available in Method 218.1 of Methods for Chemical Analysis of Water and Wastes.

9.4 The data shown in Table 1 were obtained from records of state and contractor laboratories. The data are intended to show the precision of the combined sample preparation and analysis method.

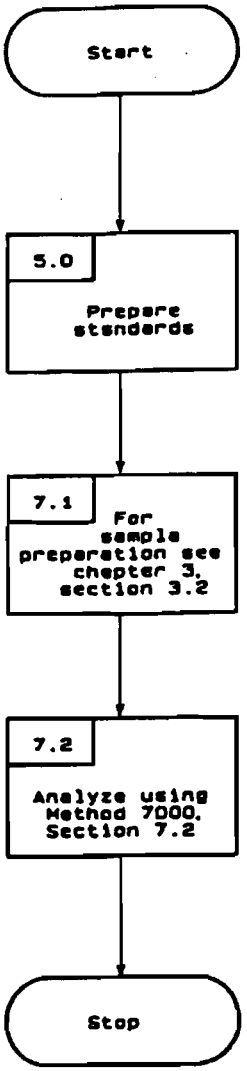
10.0 REFERENCES

1. Methods for Chemical Analysis of Water and Wastes, EPA-600/4-82-055, December 1982, Method 218.1.

2. Gaskill, A., Compilation and Evaluation of RCRA Method Performance Data, Work Assignment No. 2, EPA Contract No. 68-01-7075, September 1986.

TABLE 1. METHOD PERFORMANCE DATA

Sample Matrix	Preparation Method	Laboratory Replicates
Wastewater treatment sludge	3050	6,100, 6,000 ug/g
Emission control dust	3050	2.0, 2.8 ug/g


Start
5.0
Prepare standards
7.1
For sample preperation see chapter 3, section 3.2
7.2
Analyze using Method 7000, Section 7.2
Stop

METHOD 7191

CHROMIUM (ATOMIC ABSORPTION, FURNACE TECHNIQUE)

1.0 SCOPE AND APPLICATION

1.1 See Section 1.0 of Method 7000.

2.0 SUMMARY OF METHOD

2.1 See Section 2.0 of Method 7000.

3.0 INTERFERENCES

3.1 See Section 3.0 of Method 7000 if interferences are suspected.

3.2 Low concentrations of calcium and/or phosphate may cause interferences; at concentrations above 200 mg/L, calcium's effect is constant and eliminates the effect of phosphate. Calcium nitrate is therefore added to ensure a known constant effect.

3.3 Nitrogen should not be used as the purge gas because of a possible CN band interference.

3.4 Background correction may be required because nonspecific absorption and scattering can be significant at the analytical wavelength. Background correction with certain instruments may be difficult at this wavelength due to low-intensity output from hydrogen or deuterium lamps. Consult the specific instrument manufacturer's literature for details.

4.0 APPARATUS AND MATERIALS

4.1 For basic apparatus, see Section 4.0 of Method 7000.

4.2 Instrument parameters (general):

4.2.1 **Drying time and temp:** 30 sec at 125°C.
4.2.2 **Ashing time and temp:** 30 sec at 1000°C.
4.2.3 **Atomizing time and temp:** 10 sec at 2700°C.
4.2.4 **Purge gas:** Argon (nitrogen should not be used).
4.2.5 **Wavelength:** 357.9 nm.
4.2.6 **Background correction:** Not required.
4.2.7 Other operating parameters should be set as specified by the particular instrument manufacturer.

NOTE: The above concentration values and instrument conditions are for a Perkin-Elmer HGA-2100, based on the use of a 20-uL injection,

continuous-flow purge gas, and nonpyrolytic graphite. Smaller sizes of furnace devices or those employing faster rates of atomization can be operated using lower atomization temperatures for shorter time periods than the above-recommended settings.

5.0 REAGENTS

5.1 See Section 5.0 of Method 7000.

5.2 Preparation of standards:

5.2.1 **Stock solution:** Dissolve 1.923 g of chromium trioxide (CrO_3, analytical reagent grade) in Type II water, acidify with redistilled HNO_3, and dilute to 1 liter. Alternatively, procure a certified standard from a supplier and verify by comparison with a second standard.

5.2.2 Prepare dilutions of the stock solution to be used as calibration standards at the time of analysis. These standards should be prepared to contain 0.5% (v/v) HNO_3; 1 mL of 30% H_2O_2 and 1 mL of calcium nitrate solution, Section 5.2.3, may be added to lessen interferences (see Section 3.0).

5.2.3 **Calcium nitrate solution:** Dissolve 11.8 g of calcium nitrate, $Ca(NO_3)_2 \cdot 4H_2O$ (analytical reagent grade), in Type II water and dilute to 1 liter.

6.0 SAMPLE COLLECTION, PRESERVATION, AND HANDLING

6.1 See Chapter Three, Section 3.1.3, Sample Handling and Preservation.

7.0 PROCEDURE

7.1 Sample preparation: The procedures for preparation of the sample are given in Chapter Three, Section 3.2.

7.2 See Method 7000, Paragraph 7.3, Furnace Procedure. The calculation is given in Method 7000, Paragraph 7.4.

8.0 QUALITY CONTROL

8.1 See Section 8.0 of Method 7000.

9.0 METHOD PERFORMANCE

9.1 Precision and accuracy data are available in Method 218.2 of Methods for Chemical Analysis of Water and Wastes.

9.2 The performance characteristics for an aqueous sample free of interferences are:

Optimum concentration range: 5-100 ug/L.
Detection limit: 1 ug/L.

9.3 The data shown in Table 1 were obtained from records of state and contractor laboratories. The data are intended to show the precision of the combined sample preparation and analysis method.

10.0 REFERENCES

1. Methods for Chemical Analysis of Water and Wastes, EPA-600/4-82-055, December 1982, Method 218.2.

2. Gaskill, A., Compilation and Evaluation of RCRA Method Performance Data, Work Assignment No. 2, EPA Contract No. 68-01-7075, September 1986.

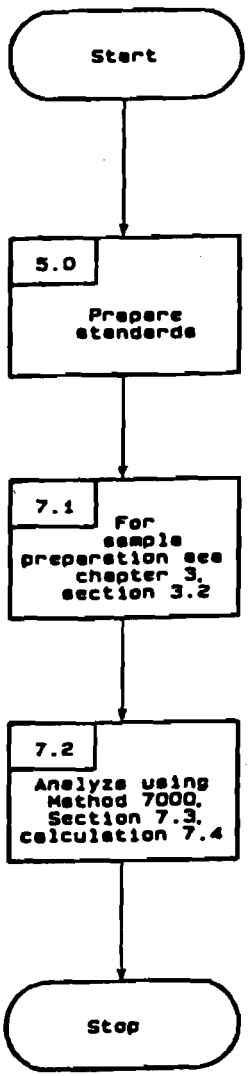
TABLE 1. METHOD PERFORMANCE DATA

Sample Matrix	Preparation Method	Laboratory Replicates
Paint primer	3050	2.7, 2.8 mg/g
Contaminated soil	3050	12.0, 12.3 ug/g
Oily lagoon soil	3050	69.6, 70.3 ug/g
NBS SRM 1646 Estuarine sediment	3050	42, 47 ug/g[a]
EPA QC Sludge	3050	156 ug/g[b]
NBS SRM 1085, Wear Metals in lubricating oil	3050	311, 356 ug/g[c]

[a]Bias of -45 and -38% from expected, respectively.

[b]Bias of -24% from expected.

[c]Bias of +4 and +19% from expected, respectively.


Start
5.0
Prepare standards
7.1
For sample preparation see chapter 3, section 3.2
7.2
Analyze using Method 7000, Section 7.3, calculation 7.4
Stop

METHOD 7195

CHROMIUM, HEXAVALENT (COPRECIPITATION)

1.0 SCOPE AND APPLICATION

1.1 Method 7195 is to be used to determine the concentration of dissolved hexavalent chromium [Cr(VI)] in Extraction Procedure (EP) toxicity characteristic extracts and ground waters. This method may also be applicable to certain domestic and industrial wastes, provided that no interfering substances are present (see Paragraph 3.1 below).

1.2 Method 7195 may be used to analyze samples containing more than 5 ug of Cr(VI) per liter. Either flame or furnace atomic absorption spectroscopy (Methods 7190 and 7191) can be used with coprecipitation.

2.0 SUMMARY OF METHOD

2.1 Method 7195 is based on the separation of Cr(VI) from solution by coprecipitation of lead chromate with lead sulfate in a solution of acetic acid. After separation, the supernate [containing Cr(III)] is drawn off and the precipitate is washed to remove occluded Cr(III). The Cr(VI) is then reduced and resolubilized in nitric acid and quantified as Cr(III) by either flame or furnace atomic absorption spectroscopy (Methods 7190 and 7191).

3.0 INTERFERENCES

3.1 Extracts containing either sulfate or chloride in concentrations above 1,000 mg/L should be diluted prior to analysis.

4.0 APPARATUS AND MATERIALS

4.1 Filtering flask: Heavy wall, 1-liter capacity.

4.2 Centrifuge tubes: Heavy duty, conical, graduated, glass-stoppered, 10-mL capacity.

4.3 Pasteur pipets: Borosilicate glass, 6.8 cm.

4.4 Centrifuge: Any centrifuge capable of reaching 2,000 rpm and accepting the centrifuge tubes described in Section 4.2 may be used.

4.5 pH meter: A wide variety of instruments are commercially available and suitable for this work.

4.6 Test tube mixer: Any mixer capable of imparting a thorough vortex is acceptable.

5.0 REAGENTS

5.1 ASTM Type II water (ASTM D1193): Water should be monitored for impurities.

5.2 Lead nitrate solution: Dissolve 33.1 g of lead nitrate, $Pb(NO_3)2$ (analytical reagent grade), in Type II water and dilute to 100 mL.

5.3 Ammonium sulfate solution: Dissolve 2.7 g of ammonium sulfate, $(NH_4)_2SO_4$ (analytical reagent grade), in Type II water and dilute to 100 mL.

5.4 Calcium nitrate solution: Dissolve 11.8 g of calcium nitrate, $Ca(NO_3)_2 \cdot 4H_2O$ (analytical reagent grade), in Type II water and dilute to 100 mL (1 mL = 20 mg Ca).

5.5 Nitric acid: Concentrated, distilled reagent grade or spectrograde quality.

5.6 Acetic acid, glacial, 10% (v/v): Dilute 10 mL glacial acetic acid, CH_3COOH (ACS reagent grade), to 100 mL with Type II water.

5.7 Ammonium hydroxide, 10% (v/v): Dilute 10 mL concentrated ammonium hydroxide, NH_4OH (analytical reagent grade), to 100 mL with Type II water.

5.8 Hydrogen peroxide, 30%: ACS reagent grade.

5.9 Potassium dichromate standard solution: Dissolve 28.285 g of dried potassium dichromate, $K_2Cr_2O_7$ (analytical reagent grade), in Type II water and dilute to 1 liter (1 mL = 10 mg Cr).

5.10 Trivalent chromium working stock solution: To 50 mL of the potassium dichromate standard solution, add 1 mL of 30% H_2O_2 and 1 mL concentrated HNO_3 and dilute to 100 mL with Type II water (1 mL = 5.0 mg trivalent chromium). Prepare fresh monthly, or as needed.

6.0 SAMPLE COLLECTION, PRESERVATION, AND HANDLING

6.1 All samples must have been collected using a sampling plan that addresses the considerations discussed in Chapter Nine of this manual.

6.2 Since the stability of Cr(VI) in EP extracts is not completely understood at this time, the analysis should be carried out as soon as possible.

6.3 To retard the chemical activity of hexavalent chromium, samples and extracts should be stored at 4°C until analyzed. The maximum holding time prior to analysis is 24 hr.

7.0 PROCEDURE

7.1 Transfer a 50-mL portion of the sample to a 100-mL Griffin beaker and adjust to a pH of 3.5 $\pm$ 0.3 by adding volumes of 10% acetic acid dropwise. Proceed immediately to Step 7.2, taking no longer than 15 min between these steps.

NOTE: Care must be exercised not to take the pH below 3. If the pH is inadvertently lowered to <3, 10% NH_4OH should be used to readjust the pH to 3.5 $\pm$ 0.3.

7.2 Pipet a 10-mL aliquot of the adjusted sample into a centrifuge tube. Add 100 uL of the lead nitrate solution, stopper the tube, mix the sample, and allow to stand for 3 min.

7.3 After the formation of lead chromate, to help retain Cr(III) complex in solution, add 0.5 mL glacial acetic acid, stopper, and mix.

7.4 To provide adequate lead sulfate for coprecipitation, add 100 uL of ammonium sulfate solution, stopper, and mix.

7.5 Place the stoppered centrifuge tube in the centrifuge, making sure that the tube is properly counterbalanced. Start the centrifuge and slowly increase the speed to 2,000 rpm in small increments over a period of 5 min. Hold at 2,000 rpm for 1 min.

NOTE: The speed of the centrifuge must be increased slowly to ensure complete coprecipitation.

7.6 After centrifuging, remove the tube and withdraw and discard the supernate using either the apparatus detailed in Figure 1 or careful decantation. If using the vacuum apparatus, the pasteur pipet is lowered into the tube and the supernate is sucked over into the filtering flask. With care, the supernate can be withdrawn to within approximately 0.1 mL above the precipitate. Wash the precipitate with 5 mL Type II water and repeat steps 7.5 and 7.6; then proceed to 7.7.

7.7 To the remaining precipitate, add 0.5 mL concentrated HNO_3, 100 uL 30% H_2O_2, and 100 uL calcium nitrate solution. Stopper the tube and mix, using a vortex mixer to disrupt the precipitate and solubilize the lead chromate. Dilute to 10 mL, mix, and analyze in the same manner as the calibration standard.

7.8 Flame atomic absorption: At the time of analysis, prepare a blank and a series of at least four calibration standards from the Cr(III) working stock that will adequately bracket the sample and cover a concentration range of 1 to 10 mg Cr/L. Add to the blank and each standard, before diluting to final volume, 1 mL 30% H_2O_2, 5 mL concentrated HNO_3, and 1 mL calcium nitrate solution for each 100 mL of prepared solution. These calibration standards should be prepared fresh weekly, or as needed. Refer to Method 7090 for more detail.

7.9 Furnace atomic absorption: At the time of analysis, prepare a blank and a series of at least four calibration standards from the Cr(III) working stock that will adequately bracket the sample and cover a concentration range of 5 to 100 ug Cr/L. Add to the blank and each standard, before diluting to final volume, 1 mL 30% H_2O_2, 5 mL concentrated HNO_3, and 1 mL calcium nitrate solution for each 100 mL of prepared solution. These calibration standards should be prepared fresh weekly, or as needed. Refer to Method 7191 for more detail.

7.10 Verification:

7.10.1 For every sample matrix analyzed, verification is required to ensure that neither a reducing condition nor chemical interference is affecting precipitation. This must be accomplished by analyzing a second 10-mL aliquot of the pH-adjusted filtrate that has been spiked with Cr(VI). The amount of spike added should double the concentration found in the original aliquot. Under no circumstance should the increase be less than 30 ug/L Cr(VI). To verify the absence of an interference, the spike recovery must be between 85% and 115%.

7.10.2 If addition of the spike extends the concentration beyond the calibration curve, the analysis solution should be diluted with blank solution and the calculated results adjusted accordingly.

7.10.3 If the result of verification indicates a suppressive interference, the sample should be diluted and reanalyzed. If necessary, use furnace atomic absorption to achieve the optimal concentration range.

7.10.4 If the interference persists after sample dilution, an alternative method (Method 7197, Chelation/Extraction, or Method 7196, Colorimetric) should be used.

7.11 Acidic extracts that yield recoveries of less than 85% should be retested to determine if the low spike recovery is due to the presence of residual reducing agent. This determination shall be performed by first making an aliquot of the extract alkaline (pH 8.0-8.5) using 1 N sodium hydroxide and then respiking and analyzing. If a spike recovery of 85-115% is obtained in the alkaline aliquot of an acidic extract that initially was found to contain less than 5 mg/L Cr(VI), one can conclude that the analytical method has been verified.

8.0 QUALITY CONTROL

8.1 All quality control data should be maintained and available for easy reference or inspection.

8.2 Calibration curves must be composed of a minimum of a blank and three standards. A calibration curve should be made for every hour of continuous sample analysis.

8.3 Dilute samples if they are more concentrated than the highest standard or if they fall on the plateau of a calibration curve.

8.4 Employ a minimum of one blank per sample batch to determine if contamination or any memory effects are occurring.

8.5 Verify calibration with an independently prepared check standard every 15 samples.

8.6 Run one spike duplicate sample for every 10 samples. A duplicate sample is a sample brought through the whole sample preparation and analytical process.

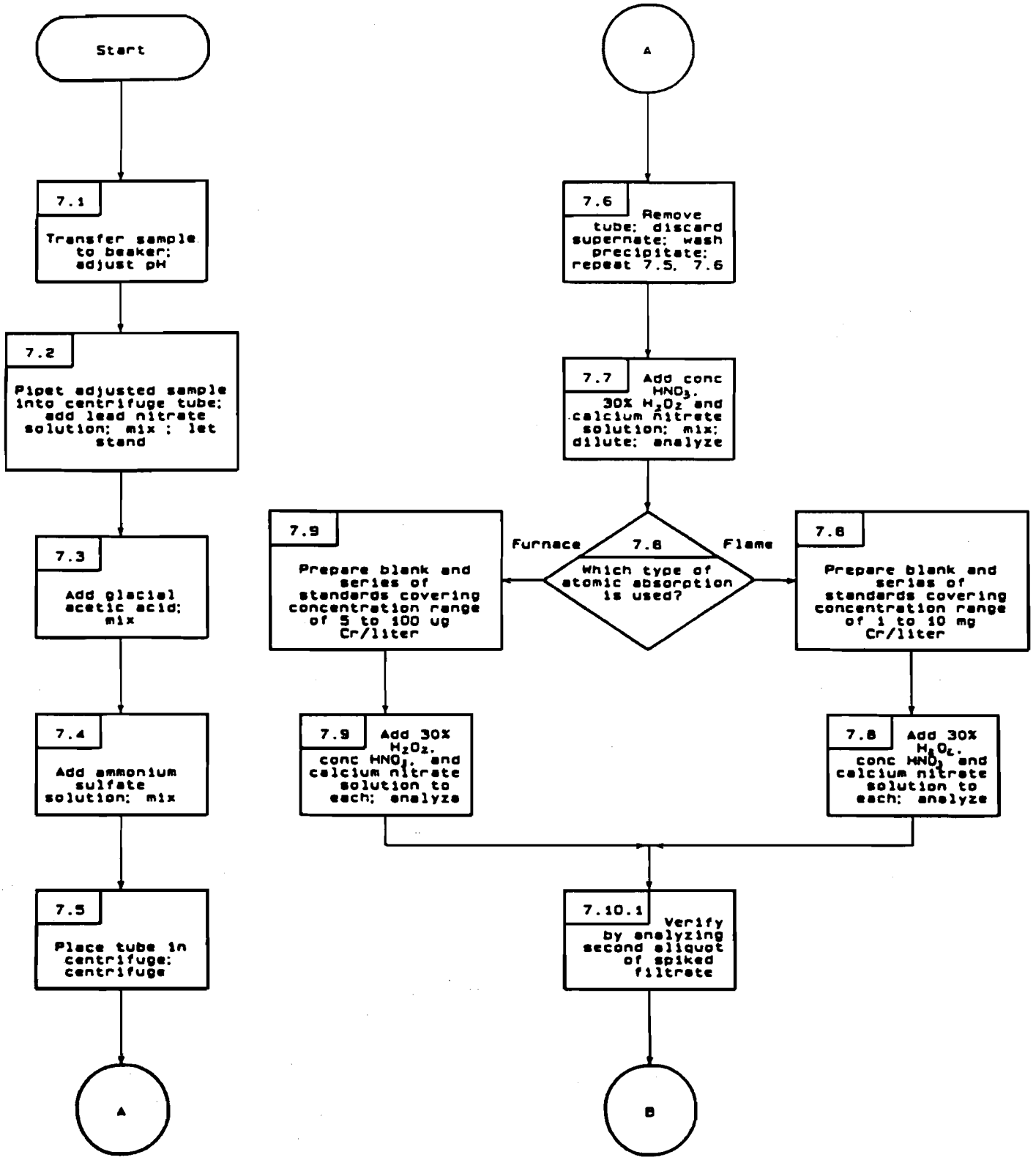
8.7 The method of standard additions (see Method 7000, Section 8.7) shall be used for the analysis of all EP extracts, on all analyses submitted as part of a delisting petition, and whenever a new sample matrix is being analyzed.

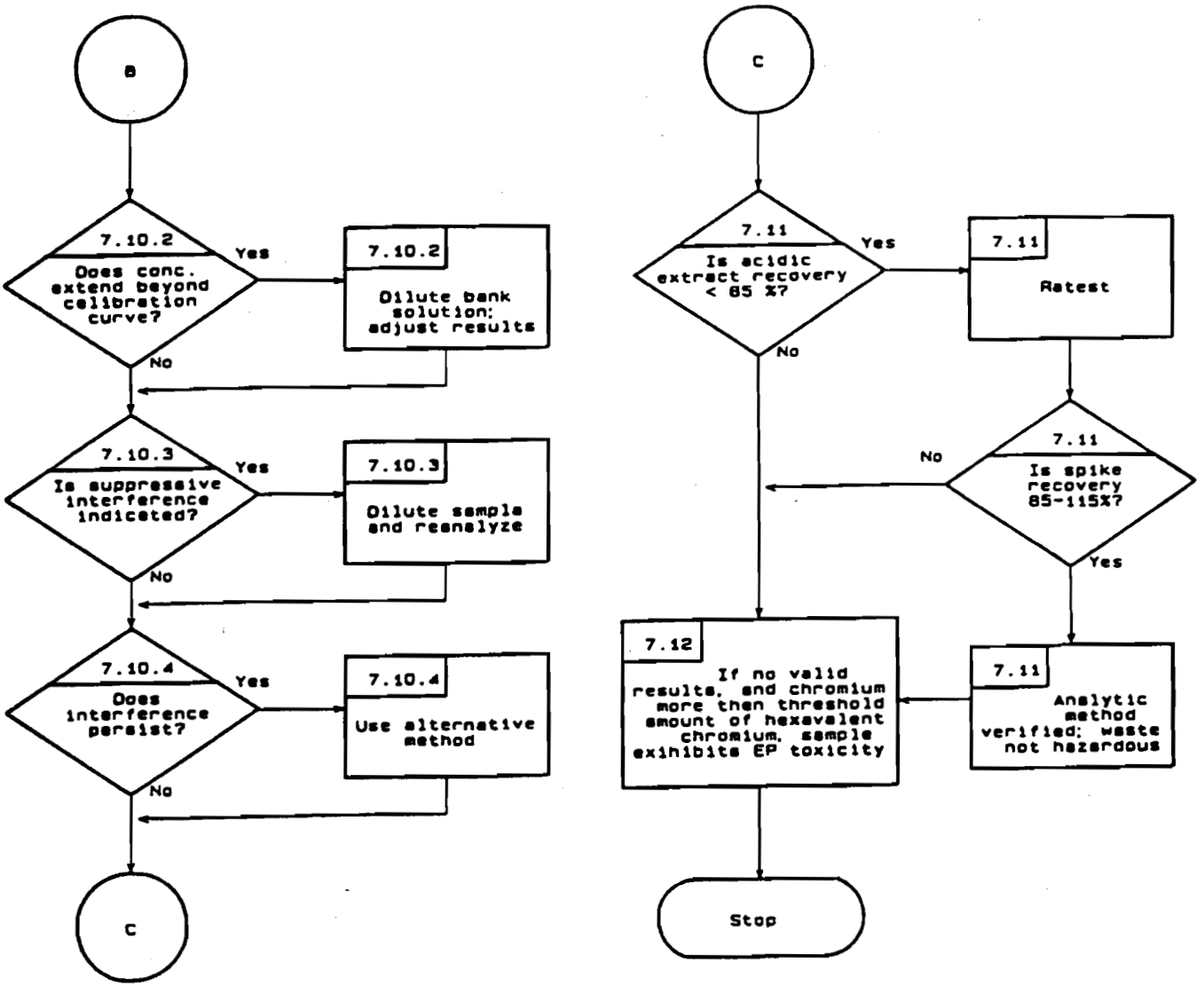
9.0 METHOD PERFORMANCE

9.1 Precision and accuracy data are available in Method 218.5 of Methods for Chemical Analysis of Water and Wastes.

10.0 REFERENCES

1. Methods for Chemical Analysis of Water and Wastes, EPA-600/4-82-055, December 1982, Method 218.5.


Start
7.1
Transfer sample to beaker; adjust pH
7.2
Pipet adjusted sample into centrifuge tube; add lead nitrate solution; mix ; let stand
7.3
Add glacial acetic acid; mix
7.4
Add ammonium sulfate solution; mix
7.5
Place tube in centrifuge; centrifuge
A
A
7.6
Remove tube; discard supernate; wash precipitate; repeat 7.5, 7.6
7.7
Add conc HNO_3, 30% H_2O_2 and calcium nitrate solution; mix; dilute; analyze
7.8
Which type of atomic absorption is used?
Furnace
Flame
7.9
Prepare blank and series of standards covering concentration range of 5 to 100 ug Cr/liter
7.8
Prepare blank and series of standards covering concentration range of 1 to 10 mg Cr/liter
7.9
Add 30% H_2O_2, conc HNO_3, and calcium nitrate solution to each; analyze
7.8
Add 30% H_2O_2, conc HNO_3, and calcium nitrate solution to each; analyze
7.10.1
Verify by analyzing second aliquot of spiked filtrate
B


B
7.10.2
Does conc. extend beyond calibration curve?
Yes
7.10.2
Dilute bank solution; adjust results
No
7.10.3
Is suppressive interference indicated?
Yes
7.10.3
Dilute sample and reanalyze
No
7.10.4
Does interference persist?
Yes
7.10.4
Use alternative method
No
C
C
7.11
Is acidic extract recovery < 85 %?
Yes
7.11
Retest
No
7.11
Is spike recovery 85-115%?
No
Yes
7.12
If no valid results, and chromium more than threshold amount of hexavalent chromium, sample exhibits EP toxicity
7.11
Analytic method verified; waste not hazardous
Stop

METHOD 7196A

CHROMIUM, HEXAVALENT (COLORIMETRIC)

1.0 SCOPE AND APPLICATION

1.1 Method 7196 is used to determine the concentration of dissolved hexavalent chromium [Cr(VI)] in EP/TCLP characteristic extracts and ground waters. This method may also be applicable to certain domestic and industrial wastes, provided that no interfering substances are present (see Paragraph 3.1 below).

1.2 Method 7196 may be used to analyze samples containing from 0.5 to 50 mg of Cr(VI) per liter.

2.0 SUMMARY OF METHOD

2.1 Dissolved hexavalent chromium, in the absence of interfering amounts of substances such as molybdenum, vanadium, and mercury, may be determined colorimetrically by reaction with diphenylcarbazide in acid solution. A red-violet color of unknown composition is produced. The reaction is very sensitive, the absorbancy index per gram atom of chromium being about 40,000 at 540 nm. Addition of an excess of diphenylcarbazide yields the red-violet product, and its absorbance is measured photometrically at 540 nm.

3.0 INTERFERENCES

3.1 The chromium reaction with diphenylcarbazide is usually free from interferences. However, certain substances may interfere if the chromium concentration is relatively low. Hexavalent molybdenum and mercury salts also react to form color with the reagent; however, the red-violet intensities produced are much lower than those for chromium at the specified pH. Concentrations of up to 200 mg/L of molybdenum and mercury can be tolerated. Vanadium interferes strongly, but concentrations up to 10 times that of chromium will not cause trouble.

3.2 Iron in concentrations greater than 1 mg/L may produce a yellow color, but the ferric iron color is not strong and difficulty is not normally encountered if the absorbance is measured photometrically at the appropriate wavelength.

4.0 APPARATUS AND MATERIALS

4.1 Colorimetric equipment: One of the following is required: Either a spectrophotometer, for use at 540 nm, providing a light path of 1 cm or longer, or a filter photometer, providing a light path of 1 cm or longer and equipped with a greenish-yellow filter having maximum transmittance near 540 nm.

5.0 REAGENTS

5.1 Reagent water: Reagent water should be monitored for impurities.

5.2 Potassium dichromate stock solution: Dissolve 141.4 mg of dried potassium dichromate, $K_2Cr_2O_7$ (analytical reagent grade), in reagent water and dilute to 1 liter (1 mL = 50 ug Cr).

5.3 Potassium dichromate standard solution: Dilute 10.00 mL potassium dichromate stock solution to 100 mL (1 mL = 5 ug Cr).

5.4 Sulfuric acid, 10% (v/v): Dilute 10 mL of distilled reagent grade or spectrograde quality sulfuric acid, H_2SO_4, to 100 mL with reagent water.

5.5 Diphenylcarbazide solution: Dissolve 250 mg 1,5-diphenylcarbazide in 50 mL acetone. Store in a brown bottle. Discard when the solution becomes discolored.

5.6 Acetone (analytical reagent grade): Avoid or redistill material that comes in containers with metal or metal-lined caps.

6.0 SAMPLE COLLECTION, PRESERVATION, AND HANDLING

6.1 All samples must have been collected using a sampling plan that addresses the considerations discussed in Chapter Nine of this manual.

6.2 Since the stability of Cr(VI) in extracts is not completely understood at this time, the analysis should be carried out as soon as possible.

6.3 To retard the chemical activity of hexavalent chromium, the samples and extracts should be stored at 4°C until analyzed. The maximum holding time prior to analysis of the samples or extracts is 24 hr. The 24 hr holding time begins after extraction.

7.0 PROCEDURE

7.1 Color development and measurement: Transfer 95 mL of the extract to be tested to a 100-mL volumetric flask. Add 2.0 mL diphenylcarbazide solution and mix. Add H_2SO_4 solution to give a pH of 2 $\pm$ 0.5, dilute to 100 mL with reagent water, and let stand 5 to 10 min for full color development. Transfer an appropriate portion of the solution to a 1-cm absorption cell and measure its absorbance at 540 nm. Use reagent water as a reference. Correct the absorbance reading of the sample by subtracting the absorbance of a blank carried through the method (see Note below). An aliquot of the sample containing all reagents except diphenylcarbazide should be prepared and used to correct the sample for turbidity (i.e., a turbidity blank). From the corrected absorbance, determine the mg/L of chromium present by reference to the calibration curve.

NOTE: If the solution is turbid after dilution to 100 mL in Step 7.1, above, take an absorbance reading before adding the carbazide

reagent and correct the absorbance reading of the final colored solution by subtracting the absorbance measured previously.

7.2 Preparation of calibration curve:

7.2.1 To compensate for possible slight losses of chromium during digestion or other operations of the analysis, treat the chromium standards by the same procedure as the sample. Accordingly, pipet a chromium standard solution in measured volumes into 250-mL beakers or conical flasks to generate standard concentrations ranging from 0.5 to 5 mg/L Cr(VI) when diluted to the appropriate volume.

7.2.2 Develop the color of the standards as for the samples. Transfer a suitable portion of each colored solution to a 1-cm absorption cell and measure the absorbance at 540 nm. As reference, use reagent water. Correct the absorbance readings of the standards by subtracting the absorbance of a reagent blank carried through the method. Construct a calibration curve by plotting corrected absorbance values against mg/L of Cr(VI).

7.3 Verification:

7.3.1 For every sample matrix analyzed, verification is required to ensure that neither a reducing condition nor chemical interference is affecting color development. This must be accomplished by analyzing a second 10-mL aliquot of the pH-adjusted filtrate that has been spiked with Cr(VI). The amount of spike added should double the concentration found in the original aliquot. Under no circumstances should the increase be less than 30 μg Cr(VI)/liter. To verify the absence of an interference, the spike recovery must be between 85% and 115%.

7.3.2 If addition of the spike extends the concentration beyond the calibration curve, the analysis solution should be diluted with blank solution and the calculated results adjusted accordingly.

7.3.3 If the result of verification indicates a suppressive interference, the sample should be diluted and reanalyzed.

7.3.4 If the interference persists after sample dilution, an alternative method (Method 7195, Coprecipitation, or Method 7197, Chelation/Extraction) should be used.

7.4 Acidic extracts that yield recoveries of less than 85% should be retested to determine if the low spike recovery is due to the presence of residual reducing agent. This determination shall be performed by first making an aliquot of the extract alkaline (pH 8.0-8.5) using 1 N sodium hydroxide and then respiking and analyzing. If a spike recovery of 85-115% is obtained in the alkaline aliquot of an acidic extract that initially was found to contain less than 5 mg/L Cr(VI), one can conclude that the analytical method has been verified.

7.5 Analyze all extracts, all samples analyzed as part of a delisting petition, and all samples that suffer from matrix interferences by the method of standard additions (see Method 7000, Section 8.7).

8.0 QUALITY CONTROL

8.1 All quality control data should be maintained and available for easy reference or inspection. Refer to Chapter One for more information.

8.2 Dilute samples if they are more concentrated than the highest standard or if they fall on the plateau of a calibration curve.

8.3 Employ a minimum of one blank per sample batch to determine if contamination or any memory effects are occurring.

8.4 Verify calibration with an independently prepared check standard every 15 samples.

8.5 Run one matrix spike replicate or one replicate sample for every ten samples. A duplicate sample is a sample brought through the whole sample preparation and analytical process. Refer to Chapter One for more information concerning matrix spikes and matrix spike duplicates.

8.6 The method of standard additions (see Method 7000, Section 8.7) shall be used for the analysis of all extracts, on all analyses submitted as part of a delisting petition, and whenever a new sample matrix is being analyzed.

9.0 METHOD PERFORMANCE

9.1 The data shown in Table 1 were obtained from records of state and contractor laboratories. The data are intended to show the precision of the combined sample preparation and analysis method.

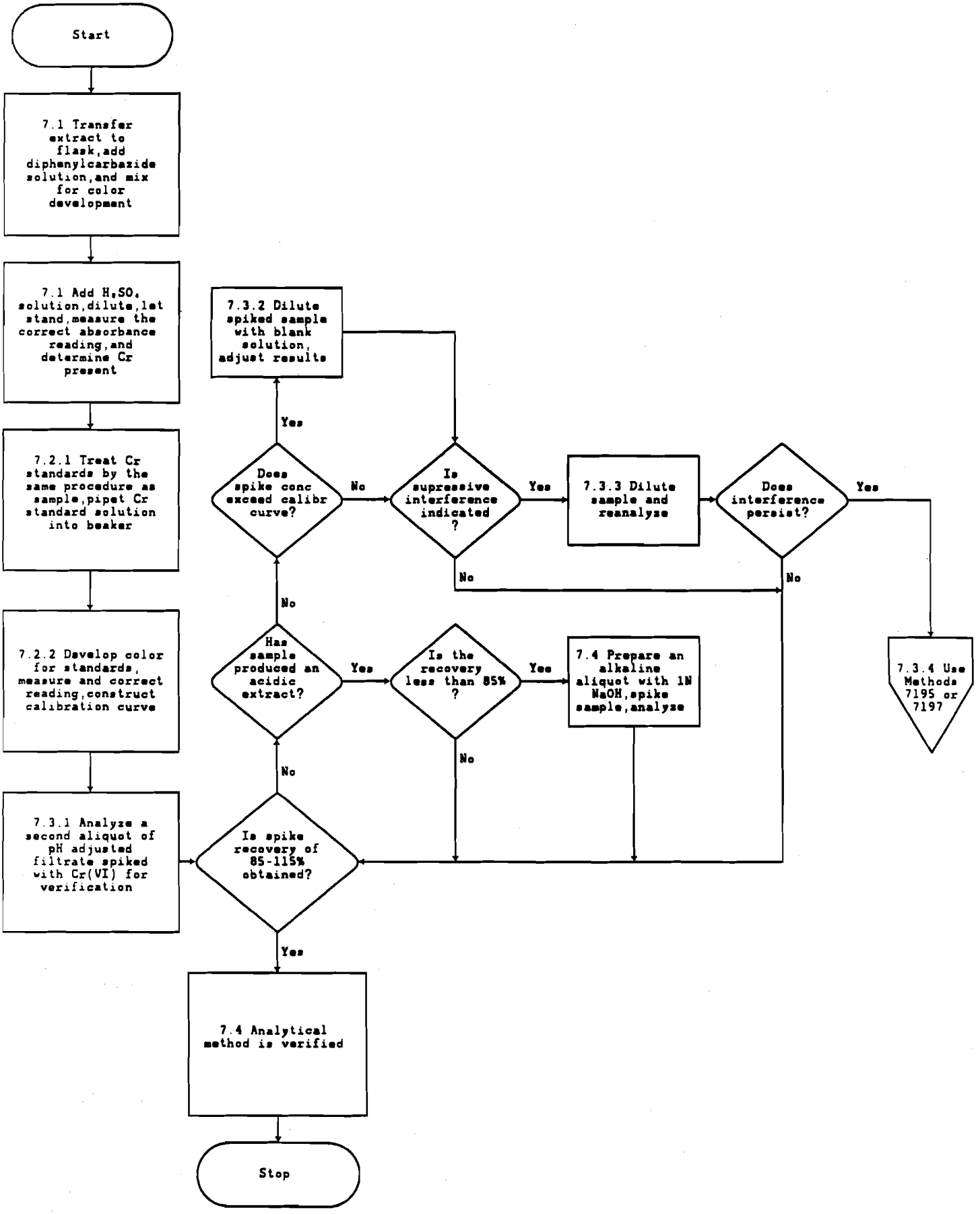
10.0 REFERENCES

1. Methods for Chemical Analysis of Water and Wastes, EPA-600/4-82-055, December 1982, Methods 218.4 and 218.5.

2. Gaskill, A., Compilation and Evaluation of RCRA Method Performance Data, Work Assignment No. 2, EPA Contract No. 68-01-7075, September 1986.

TABLE 1. METHOD PERFORMANCE DATA

Sample Matrix	Preparation Method	Laboratory Replicates
Wastewater treatment sludge	Not known	0.096, 0.107 ug/g
Sediment from chemical storage area	3060	115, 117 ug/g


Start
7.1 Transfer extract to flask, add diphenylcarbazide solution, and mix for color development
7.1 Add H_2SO_4 solution, dilute, let stand, measure the correct absorbance reading, and determine Cr present
7.2.1 Treat Cr standards by the same procedure as sample, pipet Cr standard solution into beaker
7.2.2 Develop color for standards, measure and correct reading, construct calibration curve
7.3.1 Analyze a second aliquot of pH adjusted filtrate spiked with Cr(VI) for verification
Is spike recovery of 85-115% obtained?
No
Yes
7.3.2 Dilute spiked sample with blank solution, adjust results
Does spike conc exceed calibr curve?
No
Yes
Is supressive interference indicated ?
Yes
No
7.3.3 Dilute sample and reanalyze
Does interference persist?
Yes
No
7.3.4 Use Methods 7195 or 7197
Has sample produced an acidic extract?
Yes
No
Is the recovery less than 85% ?
Yes
No
7.4 Prepare an alkaline aliquot with 1N NaOH, spike sample, analyze
7.4 Analytical method is verified
Stop

METHOD 7197

CHROMIUM, HEXAVALENT (CHELATION/EXTRACTION)

1.0 SCOPE AND APPLICATION

1.1 Method 7197 is approved for determining the concentration of dissolved hexavalent chromium [Cr(VI)] in Extraction Procedure (EP) toxicity characteristic extracts and ground waters. This method may also be applicable to certain domestic and industrial wastes, provided that no interfering substances are present (see Paragraph 3.1).

1.2 Method 7197 may be used to analyze samples containing from 1.0 to 25 ug of Cr(VI) per liter.

2.0 SUMMARY OF METHOD

2.1 Method 7197 is based on the chelation of hexavalent chromium with ammonium pyrrolidine dithiocarbamate (APDC) and extraction with methyl isobutyl ketone (MIBK). The extract is aspirated into the flame of an atomic absorption spectrophotometer.

3.0 INTERFERENCES

3.1 High concentrations of other metals may interfere.

4.0 APPARATUS AND MATERIALS

4.1 Atomic absorption spectrophotometer: Single or dual channel, single- or double-beam instrument, having a grating monochromator, photomultiplier detector, adjustable slits, and provisions for background correction.

4.2 Chromium hollow cathode lamp.

4.3 Strip-chart recorder (optional).

5.0 REAGENTS

5.1 ASTM Type II water (ASTM D1193): Water should be monitored for impurities.

5.2 Ammonium pyrrolidine dithiocarbamate (APDC) solution: Dissolve 1.0 g APDC in Type II water and dilute to 100 mL. Prepare fresh daily.

5.3 Bromphenol blue indicator solution: Dissolve 0.1 g bromphenol blue in 100 mL 50% ethanol.

5.4 Potassium dichromate standard solution I (1.0 mL = 100 ug Cr): Dissolve 0.2829 g pure dried potassium dichromate, $K_2Cr_2O_7$, in Type II water and dilute to 1,000 mL.

5.5 Potassium dichromate standard solution II (1.0 mL = 10.0 ug Cr): Dilute 100 mL chromium standard solution I to 1 liter with Type II water.

5.6 Potassium dichromate standard solution III (1.0 mL = 0.10 ug Cr): Dilute 10.0 mL chromium standard solution II to 1 liter with Type II water.

5.7 Methyl isobutyl ketone (MIBK), analytical reagent grade: Avoid or redistill material that comes in contact with metal or metal-lined caps.

5.8 Sodium hydroxide solution, 1 M: Dissolve to 40 g sodium hydroxide, NaOH (ASC reagent grade), in Type II water and dilute to 1 liter.

5.9 Sulfuric acid, 0.12 M: Slowly add 6.5 mL distilled reagent grade or spectrograde-quality sulfuric acid, H_2SO_4, to Type II water and dilute to 1 liter.

6.0 SAMPLE COLLECTION, PRESERVATION, AND HANDLING

6.1 All samples must have been collected using a sampling plan that addresses the considerations discussed in Chapter Nine of this manual.

6.2 Because the stability of Cr(VI) in EP extracts is not completely understood at this time, the chelation and extraction should be carried out as soon as possible.

6.3 To retard the chemical activity of hexavalent chromium, the samples and extracts should be stored at 4°C until analyzed.

7.0 PROCEDURE

7.1 Pipet a volume of extract containing less than 2.5 ug chromium (100 mL maximum) into a 200-mL volumetric flask and adjust the volume to approximately 100 mL.

7.2 Prepare a blank and sufficient standards and adjust the volume of each to approximately 100 mL.

7.3 Add 2 drops of bromphenol blue indicator solution. (The adjustment of pH to 2.4, Step 7.4, may be made with a pH meter instead of using an indicator.)

7.4 Adjust the pH by addition of 1 M NaOH solution dropwise until a blue color persists. Add 0.12 M H_2SO_4 dropwise until the blue color just disappears in both the standards and sample. Then add 2.0 mL of 0.12 M H_2SO_4 in excess. The pH at this point should be 2.4.

7.5 Add 5.0 mL APDC solution and mix. The pH should then be approximately 2.8.

7.6 Add 10.0 mL MIBK and shake vigorously for 3 min.

7.7 Allow the layers to separate and add Type II water until the ketone layer is completely in the neck of the flask.

7.8 Aspirate the ketone layer and record the scale reading for each sample and standard against the blank. Repeat, and average the duplicate results.

7.9 Determine the mg/liter of Cr(VI) in each sample from a plot of scale readings of standards. A working curve must be prepared with each set of samples.

7.10 Verification:

7.10.1 For every sample matrix analyzed, verification is required to ensure that neither a reducing condition nor chemical interference is affecting chelation. This must be accomplished by analyzing a second 10-mL aliquot of the pH-adjusted filtrate that has been spiked with Cr(VI). The amount of spike added should double the concentration found in the original aliquot. Under no circumstances should the increase be less than 30 ug/L Cr(VI). To verify the absence of an interference, the spike recovery must be between 85% and 115%.

7.10.2 If addition of the spike extends the concentration beyond the calibration curve, the analysis solution should be diluted with blank solution and the calculated results adjusted accordingly.

7.10.3 If the result of verification indicates a suppressive interference, the sample should be diluted and reanalyzed.

7.10.4 If the interference persists after sample dilution, an alternative method (Method 7195, Coprecipitation, or Method 7196, Colorimetric) should be used.

7.11 Acidic extracts that yield recoveries of less than 85% should be retested to determine if the low spike recovery is due to the presence of residual reducing agent. This determination shall be performed by first making an aliquot of the extract alkaline (pH 8.0-8.5) using 1 N sodium hydroxide and then respiking and analyzing. If a spike recovery of 85-115% is obtained in the alkaline aliquot of an acidic extract that initially was found to contain less than 5 mg/L Cr(VI), one can conclude that the analytical method has been verified.

8.0 QUALITY CONTROL

8.1 All quality control data should be maintained and available for easy reference or inspection.

8.2 Calibration curves must be composed of a minimum of a blank and three standards. A calibration curve should be made for every hour of continuous sample analysis.

8.3 Dilute samples if they are more concentrated than the highest standard or if they fall on the plateau of a calibration curve.

8.4 Employ a minimum of one blank per sample batch to determine if contamination or any memory effects are occurring.

8.5 Verify calibration with an independently prepared check standard every 15 samples.

8.6 Run one spike duplicate sample for every 10 samples. A duplicate sample is a sample brought through the whole sample preparation and analytical process.

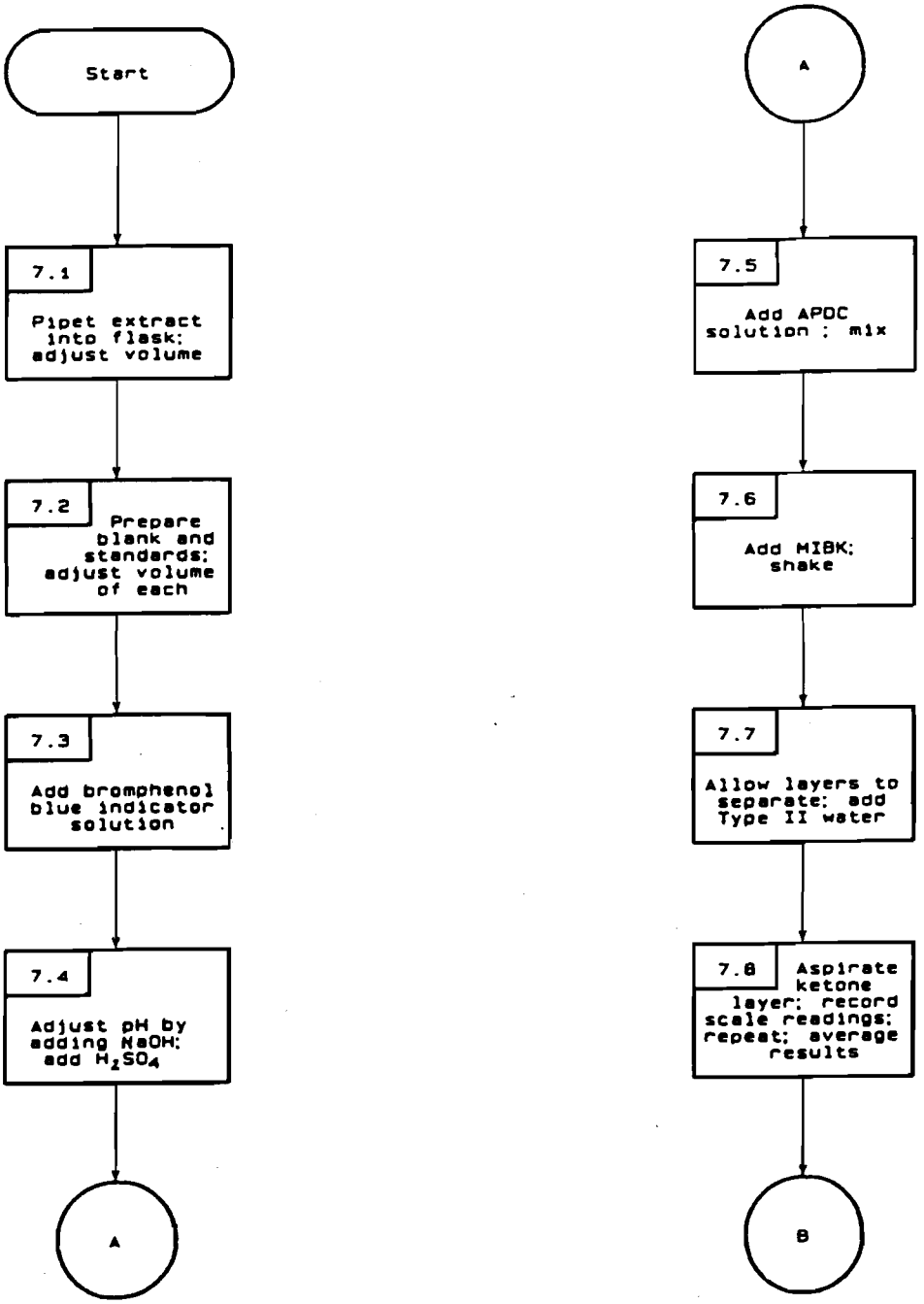
8.7 The method of standard additions (see Method 7000, Section 8.7) shall be used for the analysis of all EP extracts, on all analyses submitted as part of a delisting petition, and whenever a new sample matrix is being analyzed.

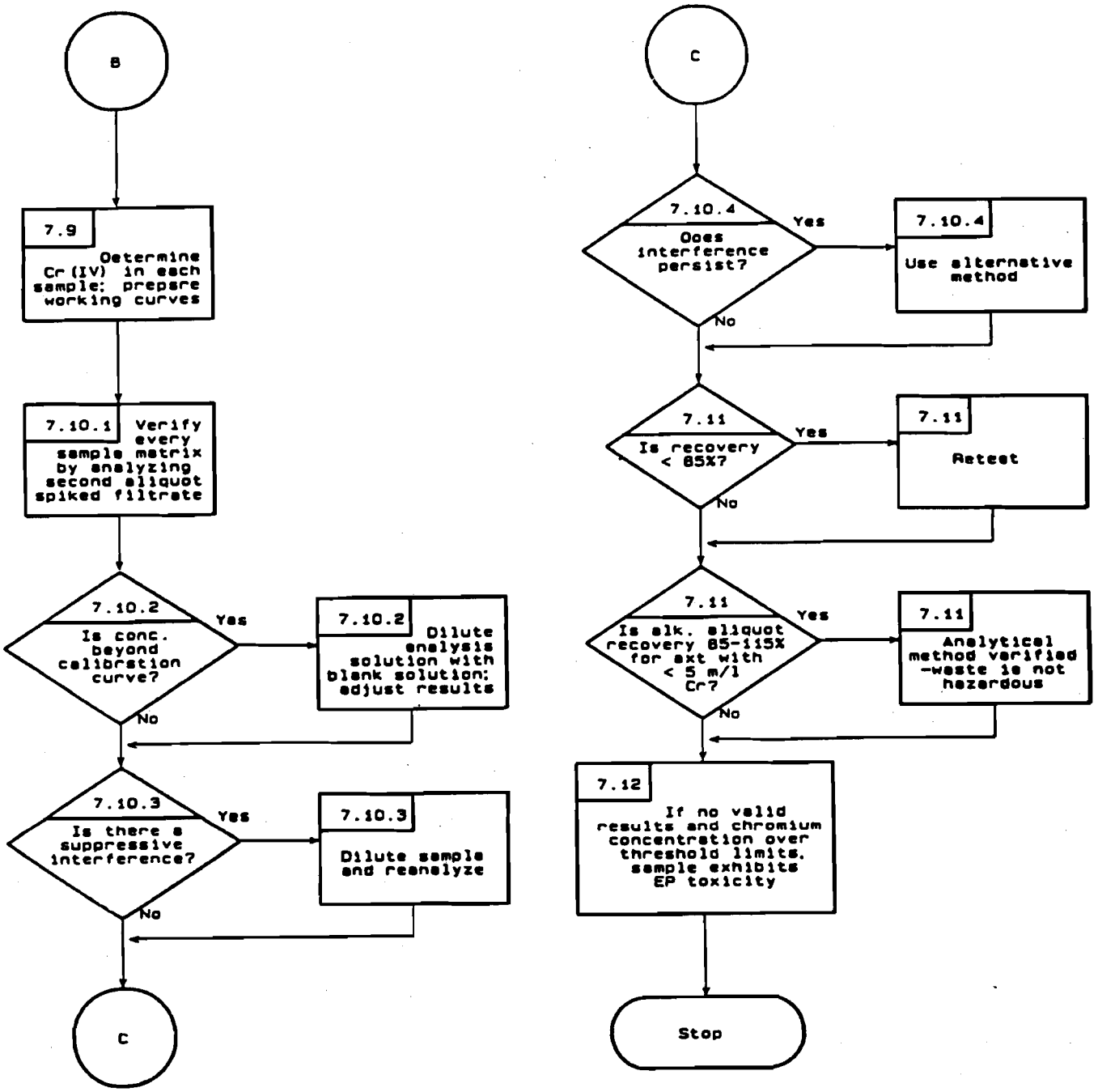
9.0 METHOD PERFORMANCE

9.1 Precision and accuracy data are available in Method 218.4 of Methods for Chemical Analysis of Water and Wastes.

10.0 REFERENCES

1. Methods for Chemical Analysis of Water and Wastes, EPA-600/4-82-055, December 1982, Method 218.4.


Start
7.1
Pipet extract into flask; adjust volume
7.2
Prepare blank and standards; adjust volume of each
7.3
Add bromphenol blue indicator solution
7.4
Adjust pH by adding NaOH; add H_2SO_4
A
A
7.5
Add APDC solution ; mix
7.6
Add MIBK; shake
7.7
Allow layers to separate; add Type II water
7.8
Aspirate ketone layer; record scale readings; repeat; average results
B


B
7.9
Determine Cr(IV) in each sample; prepare working curves
7.10.1
Verify every sample matrix by analyzing second aliquot spiked filtrate
7.10.2
Is conc. beyond calibration curve?
Yes
No
7.10.2
Dilute analysis solution with blank solution; adjust results
7.10.3
Is there a suppressive interference?
Yes
No
7.10.3
Dilute sample and reanalyze
C
C
7.10.4
Does interference persist?
Yes
No
7.10.4
Use alternative method
7.11
Is recovery < 85%?
Yes
No
7.11
Retest
7.11
Is alk. aliquot recovery 85-115% for ext with < 5 m/l Cr?
Yes
No
7.11
Analytical method verified -waste is not hazardous
7.12
If no valid results and chromium concentration over threshold limits, sample exhibits EP toxicity
Stop

METHOD 7198

CHROMIUM, HEXAVALENT (DIFFERENTIAL PULSE POLAROGRAPHY)

1.0 SCOPE AND APPLICATION

1.1 This method is used to determine the concentration of hexavalent chromium [Cr(VI)] in natural and waste waters and in EP extracts.

1.2 The method can quantitate chromium in concentrations of up to 1.0 mg/L to 5.0 mg/L, depending on the mercury drop size. Higher concentrations can be determined by dilution.

1.3 The lower limit of detection for Cr(VI) is 10 ug/L for the instrumental conditions given in this method. The limit of detection could be easily lowered by changing these conditions.

2.0 SUMMARY OF METHOD

2.1 Method 7198 measures the peak current produced from the reduction of Cr(VI) to Cr(III) at a dropping mercury electrode during a differential pulse voltage ramp.

2.2 The method described herein uses 0.125 M NH_4OH-0.125 M NH_4Cl as the supporting electrolyte. In this electrolyte, Cr(VI) reduction results in peak current occurring at the peak potential (Ep) of -0.250 V vs. Ag/AgCl.

2.3 Alternative supporting electrolytes, such as those given in Table 1, may be used.

2.4 The technique of standard additions must be used to quantitate the Cr(VI) content.

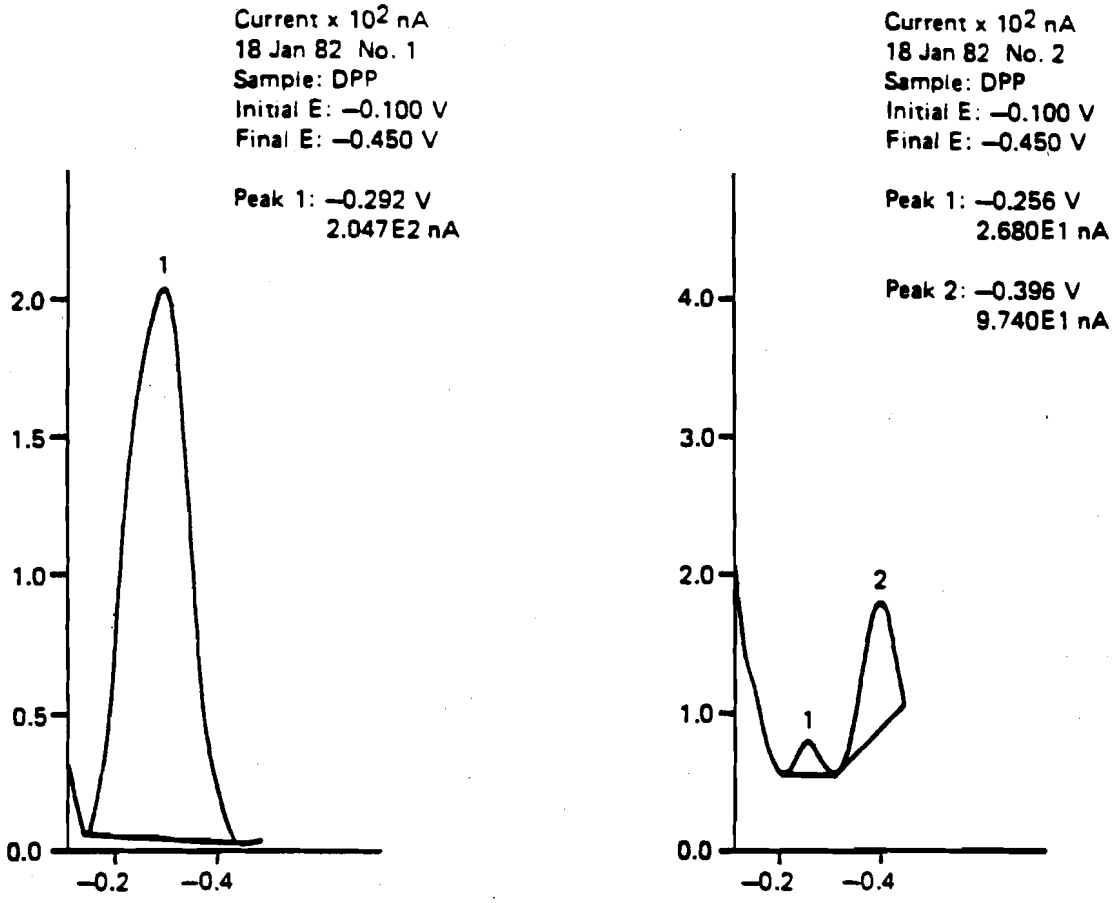
3.0 INTERFERENCES

3.1 Copper ion at concentrations higher than the Cr(VI) concentration is a potential interference due to peak overlap when using the 0.125 M ammoniacal electrolyte. Increasing the ammoniacal electrolyte concentration to 0.5 M shifts the copper peak cathodically (Ep = -0.4 V), eliminating the interference at a copper-to-chromium ratio of 10:1 (Figure 1).

3.2 Reductants such as ferrous iron, sulfite, and sulfide will reduce Cr(VI) to Cr(III); thus it is imperative to analyze the samples as soon as possible.

4.0 APPARATUS AND MATERIALS

4.1 Polarographic instrumentation: Capable of performing differential pulse analyses, including recorder or plotter.



A. 20 ppm Cu, 2.5 ppm Cr, 0.1 N buffer.

B. 20 ppm Cu, 2.5 ppm Cr, 0.5 N buffer.

Figure 1. Two polarograms illustrating shift in copper peak at higher ammoniacal electrolyte concentrations.

TABLE 1. POLAROGRAPHY OF HEXAVALENT CHROMIUM

Supporting electrolyte	Peak potential (vs. SCE)
1 M NaOH	-0.85
1 M Pyridine, 1 M NaOH	-1.48
1 M NH_4OH, 1 M NH_4Cl	-0.36
0.1 M NH_4OH, 0.1 M $(NH_4)_2$ Tartrate	-0.244
0.2 M KCl, 0.3 M Triethanolamine, pH 9	-0.28
1 M Na_2SO_4	-0.23
0.1 M NH_4OH, 0.1 M NH_4Cl	-0.25

4.2 Dropping mercury electrode assembly: Capable of performing differential pulse analyses.

4.3 Counter electrode: Platinum wire.

4.4 Reference electrode: Ag/AgCl or SCE, with a slow-leakage fritted tip (unfired Vycor).

4.5 Nitrogen gas and cell outgassing assembly.

4.6 Micropipets and disposable tips.

5.0 REAGENTS

5.1 ASTM Type II water (ASTM D1193): Water should be monitored for impurities.

5.2 Chromium standard solution I, 1.0 mL = 100 ug Cr: Should be made daily from a 1,000-ppm standard stock solution made with Type II water.

5.3 Chromium standard solution II, 1.0 mL = 10 ug Cr: Should be made daily from a 1,000-ppm standard stock solution made with Type II water.

5.4 Chromium standard solution III, 1.0 mL = 1 ug Cr: Dilute 10 mL chromium standard solution II to 100 mL with Type II water.

5.5 Ammoniacal electrolyte, 2.5 N: Dissolve 33.3 g of NH_4Cl in 150 mL of Type II water, add 42.2 mL of concentrated NH_4OH, and dilute to 250 mL.

5.6 Concentrated nitric acid: Acid should be analyzed to determine levels of impurities. If impurities are detected, all analyses should be blank-corrected.

6.0 SAMPLE COLLECTION, PRESERVATION, AND HANDLING

6.1 All samples must have been collected using a sampling plan that addresses the considerations discussed in Chapter Nine of this manual.

6.2 Stability of Cr(VI) is not completely understood at this time. Therefore, the analysis should be carried out as soon as possible.

6.3 If the analysis cannot be performed within 24 hr, take an aliquot of the sample and add a known amount of Cr(VI) (0.1 mg/L for natural waters, 1 mg/L for wastewaters, and 5 mg/L for EP extracts). Analyze this known additional sample at the same time the sample is analyzed to determine whether Cr(VI) was reduced during storage.

6.4 To retard the chemical activity of Cr(VI), the sample should be transported and stored at 4°C until time of analysis.

7.0 PROCEDURE

7.1 Soak the voltammetric cells overnight in 1 + 1 HNO_3 and/or 1 + 1 aqua regia.

7.2 Rinse the electrode assembly with Type II water, then with 1 N HNO_3, and finally with Type II water prior to and in between sample analyses.

7.3 The instrument should be set using the following instrumental parameters.

7.3.1 **Mode:** Differential pulse.
7.3.2 **Scan rate:** 2 mV/sec.
7.3.3 **Drop time:** 1 sec.
7.3.4 **Initial potential:** -0.05 V $\pm$ 0.05 V vs. Ag/AgCl.
7.3.5 **Final potential:** -0.50 V $\pm$ 0.10 V vs. Ag/AgCl.
7.3.6 **Pulse height:** 0.05 V.
7.3.7 **Deaeration time:** 240 sec or less initially, 30 sec between standard additions.

7.4 Analysis:

7.4.1 Pipet a volume of sample containing less than 10 ug Cr(VI) into a voltammetric cell (the maximum volume depends on the voltammetric cell volume, usually 10 mL).

7.4.2 Add 0.5 mL of the ammoniacal electrolyte and adjust volume to 10 mL with Type II water.

7.4.3 Place the electrode assembly in the solution and outgas with nitrogen for at least 120 sec.

7.4.4 Engage the electrode assembly to the polarographic analyzer and displace at least 10 mercury drops before initiating the voltage ramp and obtaining the polarogram.

7.4.5 Figure 2 gives typical differential pulse polarograms.

7.5 Prior to the analysis of any samples, and during analysis at a frequency of at least once every 10 samples, verify that the cell contamination is less than 10 ug/L Cr by analyzing demineralized water and the appropriate volume of supporting electrolyte in a manner similar to the procedure described in 7.4.3 and 7.4.4.

7.6 Calibration:

7.6.1 After running a differential pulse polarogram on the sample solution, quantitate the chromium using the technique of standard addition.

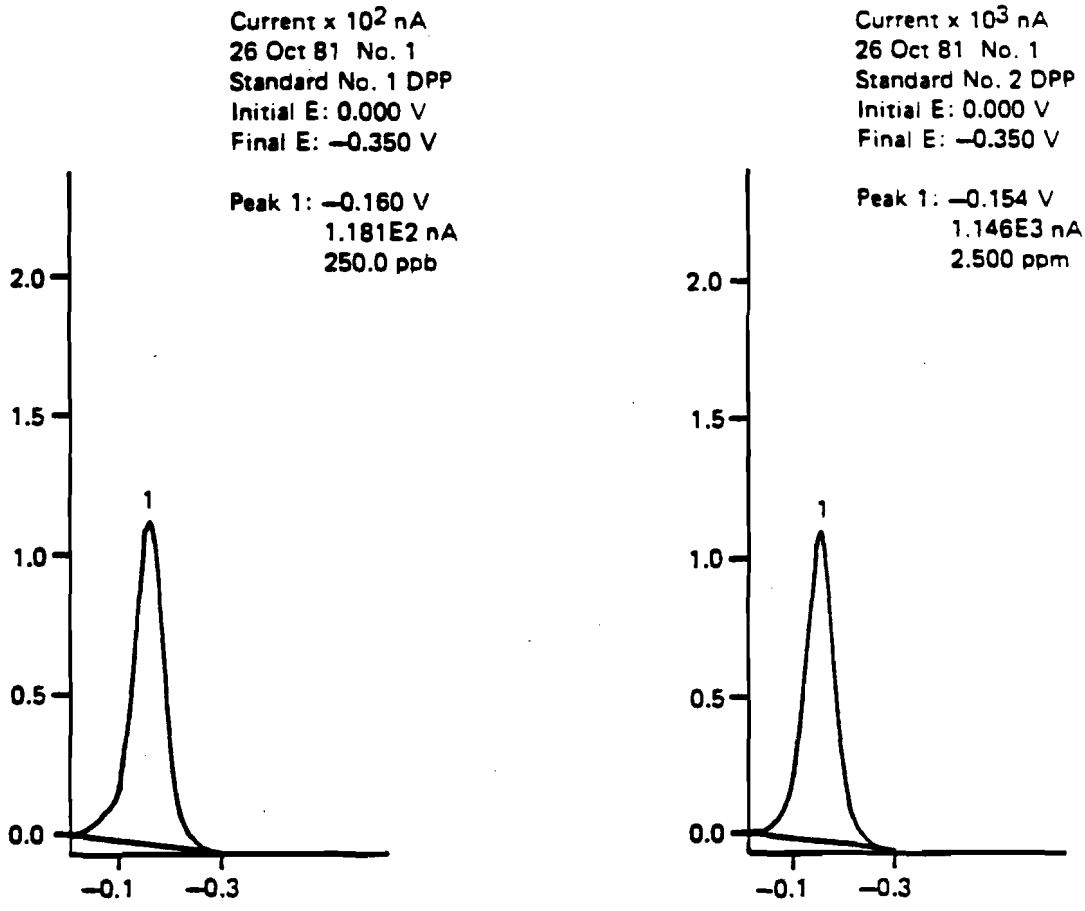


Figure 2. Typical differential pulse polarogram at 0.25 ppm and 2.5 ppm Cr in 0.1 N buffer.

7.6.2 Three standard additions should be made to obtain the best precision and accuracy. The first standard addition should be approximately one-half the concentration of the sample, the second equal to that of the sample, and the third about 1.5 times the sample concentration. The total volume due to standard additions should not exceed the cell value by more than 10%.

7.6.3 Add an appropriate aliquot of chromium standard solution I, II, or III to the sample in the cell. Deaerate for 30 sec to mix the solution and remove oxygen added with the known addition.

7.6.4 Repeat the analysis procedure, beginning with Step 7.4.4 for each standard addition.

7.7 Calculations:

7.7.1 Calculate the concentration of chromium determined by each standard addition procedure as follows:

$$C_u = \frac{i_1 V_f C_s}{i_1 V_f + (i_1 - i_f)V} \times \frac{V}{V_u}$$

where:

i_1 = Current peak height for the sample (nA);

i_f = Current peak height for the sample plus standard (nA);

V_u = Volume of sample in the cell (mL);

V_f = Volume of standard taken for spiking (mL);

V = Volume in cell prior to standard addition;

C_s = Concentration of standard used to spike (mg/L); and

C_u = Concentration of the unknown in the sample (mg/L).

7.7.2 Some microprocessor polarographic systems will perform these calculations automatically.

8.0 QUALITY CONTROL

8.1 All quality control data should be maintained and available for easy reference or inspection.

8.2 If necessary, dilute samples so that they fall within the working range.

8.3 Quantitation must be performed by the method of standard additions (see Method 7000, Section 8.7).

8.4 Verify calibration with an independently prepared check standard every 15 samples (see Chapter One, Section 1.1.8).

8.5 Standards should be compared to a reference standard on a routine basis.

9.0 METHOD PERFORMANCE

9.1 Precision and accuracy data for this method are summarized in Table 2.

10.0 REFERENCES

1. Methods for Chemical Analysis of Water and Wastes, EPA-600/4-82-055, December 1982, Method 218.4 and 218.5.

TABLE 2. PRECISION AND ACCURACY OF THE DPP OF HEXAVALENT CHROMIUM

2a. Precision

Sample type	No. of replicates	Average value	% RSD
Leachate[a]	3	1.87	0.69

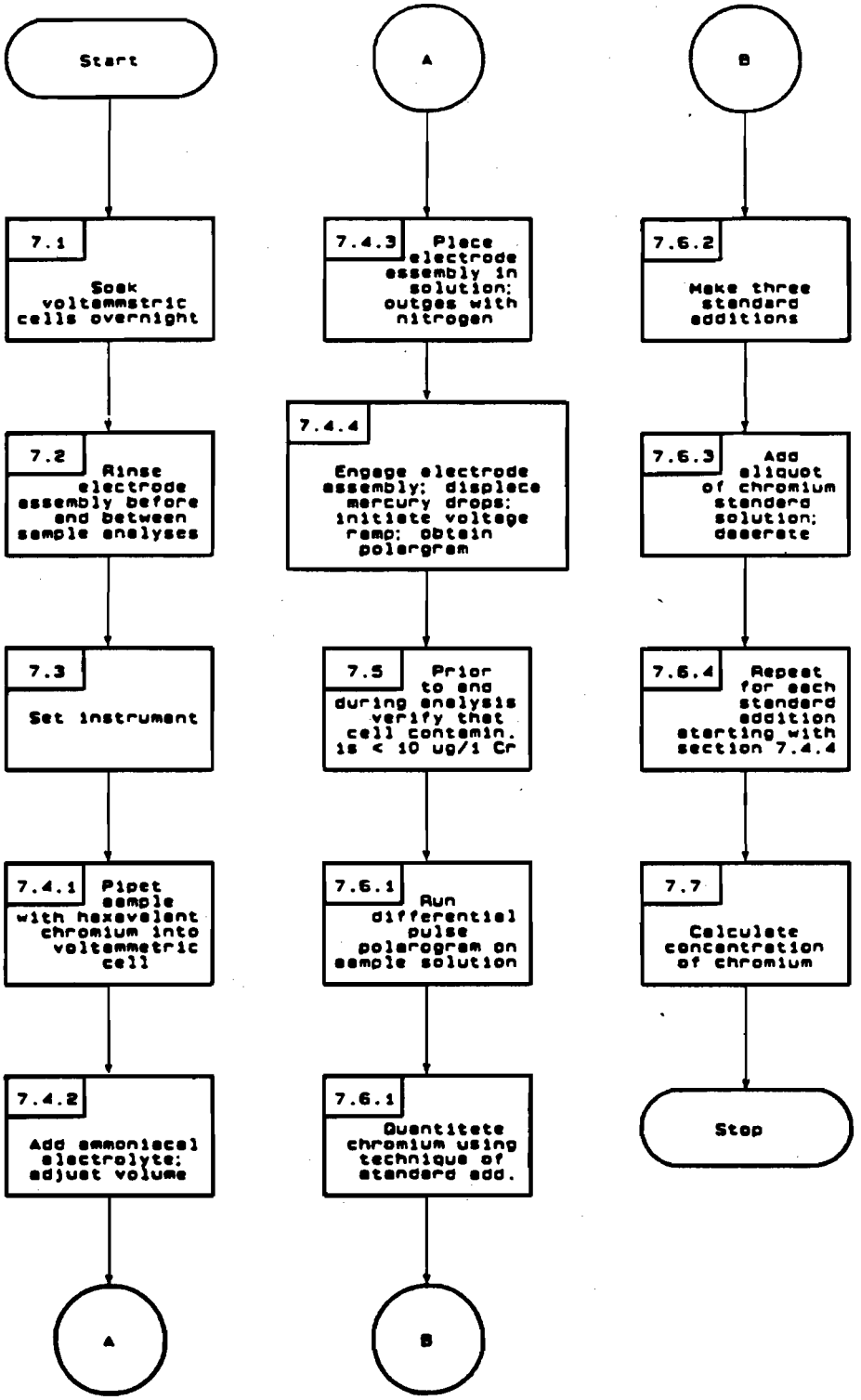
2b. Accuracy (spike recovery data)

Sample type	Spike level (mg/L)	No. of samples	Average % recovery	Standard deviation of % recovery
EP extracts	5.0	8	92.8	6.4

2c. Methods comparison

	Diff. pulse polarography	APDC extraction ICAP-OES	Ion chromatography coupled to ICAP-OES
Value[a]	1.87	1.84	1.91

[a]Leachate sample from a waste disposal site.


Start
7.1 Soak voltammetric cells overnight
7.2 Rinse electrode assembly before and between sample analyses
7.3 Set instrument
7.4.1 Pipet sample with hexavalent chromium into voltammetric cell
7.4.2 Add ammoniacal electrolyte; adjust volume
A
A
7.4.3 Place electrode assembly in solution; purges with nitrogen
7.4.4 Engage electrode assembly; displace mercury drops; initiate voltage ramp; obtain polergram
7.5 Prior to and during analysis verify that cell contamin. is < 10 ug/l Cr
7.6.1 Run differential pulse polarogram on sample solution
7.6.1 Quantitate chromium using technique of standard add.
B
B
7.6.2 Make three standard additions
7.6.3 Add aliquot of chromium standard solution; deaerate
7.6.4 Repeat for each standard addition starting with section 7.4.4
7.7 Calculate concentration of chromium
Stop

METHOD 7200

COBALT (ATOMIC ABSORPTION, DIRECT ASPIRATION)

1.0 SCOPE AND APPLICATION

1.1 See Section 1.0 of Method 7000.

2.0 SUMMARY OF METHOD

2.1 See Section 2.0 of Method 7000.

3.0 INTERFERENCES

3.1 See Section 3.0 of Method 7000 if interferences are suspected.

3.2 Excesses of other transition metals may slightly depress the response of cobalt. Matrix matching or the method of standard additions is recommended.

4.0 APPARATUS AND MATERIALS

4.1 For basic apparatus, see Section 4.0 of Method 7000.

4.2 Instrument parameters (general):

4.2.1 **Cobalt hollow cathode lamp.**
4.2.2 **Wavelength:** 240.7 nm.
4.2.3 **Fuel:** Acetylene.
4.2.4 **Oxidant:** Air.
4.2.5 **Type of flame:** Oxidizing (fuel lean).
4.2.6 **Background correction:** Required.

5.0 REAGENTS

5.1 See Section 5.0 of Method 7000.

5.2 Preparation of standards:

5.2.1 **Stock solution:** Dissolve 1.000 g of cobalt metal (analytical reagent grade) in 20 mL of 1:1 HNO_3 and dilute to 1 liter with Type II water. Chloride or nitrate salts of cobalt (II) may be used. Although numerous hydrated forms exist, they are not recommended unless the exact composition of the compound is known. Alternatively, procure a certified standard from a supplier and verify by comparison with a second standard.

5.2.2 Prepare dilutions of the stock solution to be used as calibration standards at the time of analysis. The calibration standards should be prepared using the same type of acid and at the same concentration as will result in the sample to be analyzed after processing.

6.0 SAMPLE COLLECTION, PRESERVATION, AND HANDLING

6.1 See Chapter Three, Section 3.1.3, Sample Handling and Preservation.

7.0 PROCEDURE

7.1 Sample preparation: The procedures for preparation of the sample are given in Chapter Three, Section 3.2.

7.2 See Method 7000, Paragraph 7.2, Direct Aspiration.

8.0 QUALITY CONTROL

8.1 See Section 8.0 of Method 7000.

9.0 METHOD PERFORMANCE

9.1 The performance characteristics for an aqueous sample free of interferences are:

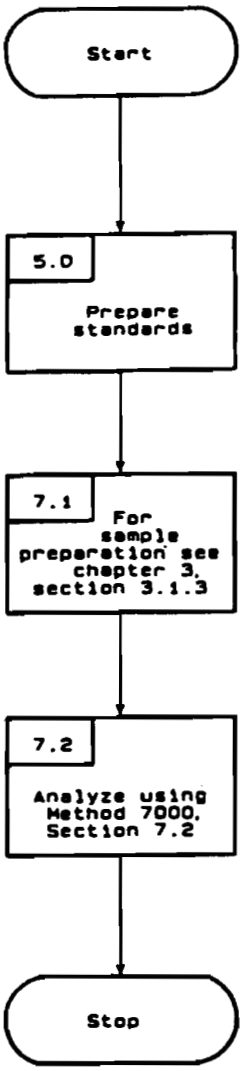
Optimum concentration range: 0.5-5 mg/L with a wavelength of 240.7 nm.
Sensitivity: 0.2 mg/L.
Detection limit: 0.05 mg/L.

9.2 In a single laboratory, analysis of a mixed industrial-domestic waste effluent, digested with Method 3010, at concentrations of 0.2, 1, and 5 mg/L gave standard deviations of $\pm$0.013, $\pm$0.01, and $\pm$0.05, respectively. Recoveries at these levels were 98% and 97%, respectively.

9.3 For concentrations of cobalt below 0.1 mg/L, the furnace procedure (Method 7201) is recommended.

10.0 REFERENCES

1. Methods for Chemical Analysis of Water and Wastes, EPA-600/4-82-055, December 1982, Method 219.1.


Start
5.0
Prepare standards
7.1
For sample preparation see chapter 3, section 3.1.3
7.2
Analyze using Method 7000, Section 7.2
Stop

METHOD 7201

COBALT (ATOMIC ABSORPTION, FURNACE TECHNIQUE)

1.0 SCOPE AND APPLICATION

1.1 See Section 1.0 of Method 7000.

2.0 SUMMARY OF METHOD

2.1 See Section 2.0 of Method 7000.

3.0 INTERFERENCES

3.1 See Section 3.0 of Method 7000 if interferences are suspected.

3.2 Excess chloride may interfere. It is necessary to verify by standard additions that the interference is absent.

4.0 APPARATUS AND MATERIALS

4.1 For basic apparatus, see Section 4.0 of Method 7000.

4.2 Instrument parameters (general):

4.2.1 Drying time and temp: 30 sec at 125°C.
4.2.2 Ashing time and temp: 30 sec at 900°C.
4.2.3 Atomizing time and temp: 10 sec at 2700°C.
4.2.4 Purge gas: Argon.
4.2.5 Wavelength: 240.7 nm.
4.2.6 Background correction: Required.
4.2.7 Other operating parameters should be set as specified by the particular instrument manufacturer.

NOTE: The above concentration values and instrument conditions are for a Perkin-Elmer HGA-2100, based on the use of a 20-uL injection, continuous-flow purge gas, and nonpyrolytic graphite. Smaller sizes of furnace devices or those employing faster rates of atomization can be operated using lower atomization temperatures for shorter time periods than the above-recommended settings.

5.0 REAGENTS

5.1 See Section 5.0 of Method 7000.

5.2 Preparation of standards:

5.2.1 **Stock solution:** Dissolve 1.000 g of cobalt metal (analytical reagent grade) in 20 mL of 1:1 HNO_3 and dilute to 1 liter with Type II water. Chloride or nitrate salts of cobalt (II) may be used. Although numerous hydrated forms exist, they are not recommended unless the exact composition of the compound is known. Alternatively, procure a certified standard from a supplier and verify by comparison with a second standard.

5.2.2 Prepare dilutions of the stock solution to be used as calibration standards at the time of analysis. The calibration standards should be prepared using the same type of acid and at the same concentrations as in the sample after processing (0.5% v/v HNO_3).

6.0 SAMPLE COLLECTION, PRESERVATION, AND HANDLING

6.1 See Chapter Three, Section 3.1.3, Sample Handling and Preservation.

7.0 PROCEDURE

7.1 Sample preparation: The procedures for preparation of the sample are given in Chapter Three, Section 3.2.

7.2 See Method 7000, Paragraph 7.3, Furnace Procedure.

8.0 QUALITY CONTROL

8.1 See Section 8.0 of Method 7000.

9.0 METHOD PERFORMANCE

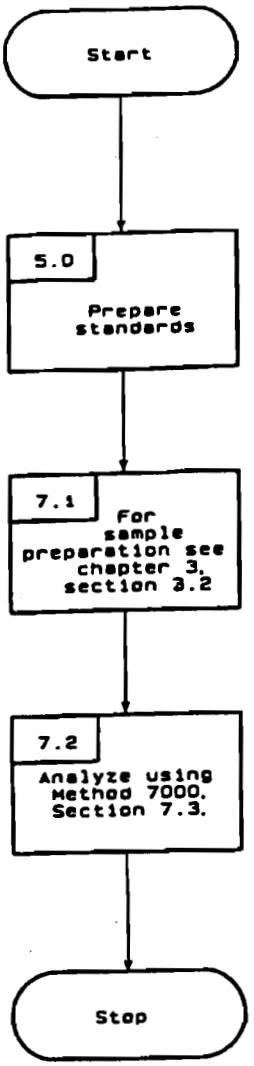
9.1 Precision and accuracy data are not available at this time.

9.2 The performance characteristics for an aqueous sample free of interferences are:

Optimum concentration range: 5-100 ug/L.
Detection limit: 1 ug/L.

10.0 REFERENCES

1. Methods for Chemical Analysis of Water and Wastes, EPA-600/4-82-055, December 1982, Method 219.2.


Start
5.0
Prepare standards
7.1
For sample preparation see chapter 3, section 3.2
7.2
Analyze using Method 7000, Section 7.3.
Stop

METHOD 7210

COPPER (ATOMIC ABSORPTION, DIRECT ASPIRATION)

1.0 SCOPE AND APPLICATION

1.1 See Section 1.0 of Method 7000.

2.0 SUMMARY OF METHOD

2.1 See Section 2.0 of Method 7000.

3.0 INTERFERENCES

3.1 See Section 3.0 of Method 7000.

3.2 Background correction may be required because nonspecific absorption and scattering can be significant at the analytical wavelength. Background correction with certain instruments may be difficult at this wavelength due to low-intensity output from hydrogen or deuterium lamps. Consult specific instrument manufacturer's literature for details.

4.0 APPARATUS AND MATERIALS

4.1 For basic apparatus, see Section 4.0 of Method 7000.

4.2 Instrument parameters (general):

4.2.1 **Copper hollow cathode lamp.**
4.2.2 **Wavelength:** 324.7 nm.
4.2.3 **Fuel:** Acetylene.
4.2.4 **Oxidant:** Air.
4.2.5 **Type of flame:** Oxidizing (fuel lean).
4.2.6 **Background correction:** Recommended, if possible.

5.0 REAGENTS

5.1 See Section 5.0 of Method 7000.

5.2 Preparation of standards:

5.2.1 **Stock solution:** Dissolve 1.00 g of electrolytic copper (analytical reagent grade) in 5 mL of redistilled HNO_3 and dilute to 1 liter with Type II water. Alternatively, procure a certified standard from a supplier and verify by comparison with a second standard.

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5.2.2 Prepare dilutions of the stock solution to be used as calibration standards at the time of analysis. The calibration standards should be prepared using the same type of acid and at the same concentration as will result in the sample to be analyzed after processing.

6.0 SAMPLE COLLECTION, PRESERVATION, AND HANDLING

6.1 See Chapter Three, Section 3.1.3, Sample Handling and Preservation.

7.0 PROCEDURE

7.1 Sample preparation: The procedures for preparation of the sample are given in Chapter Three, Section 3.2.

7.2 See Method 7000, Paragraph 7.2, Direct Aspiration.

8.0 QUALITY CONTROL

8.1 See Section 8.0 of Method 7000.

9.0 METHOD PERFORMANCE

9.1 The performance characteristics for an aqueous sample free of interferences are:

Optimum concentration range: 0.2-5 mg/L with a wavelength of 324.7 nm.
Sensitivity: 0.1 mg/L.
Detection limit: 0.02 mg/L.

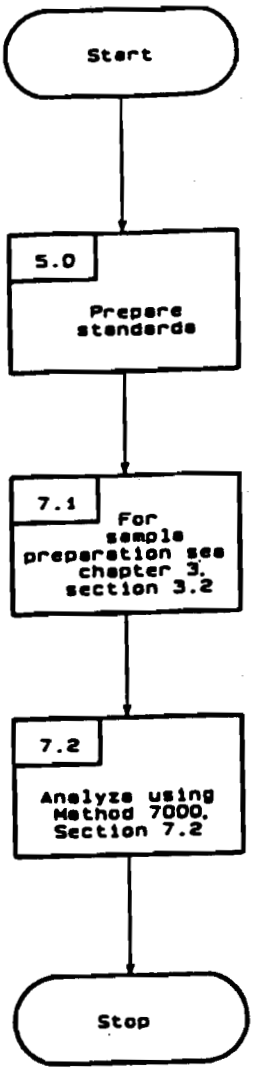
9.2 Precision and accuracy data are available in Method 220.1 of Methods for Chemical Analysis of Water and Wastes.

10.0 REFERENCES

1. Methods for Chemical Analysis of Water and Wastes, EPA-600/4-82-055, December 1982, Method 220.1.

METHOD 7210

COPPER (ATOMIC ABSORPTION, DIRECT ASPIRATION)



METHOD 7211

COPPER (ATOMIC ABSORPTION, FURNACE TECHNIQUE)

1.0 SCOPE AND APPLICATION

1.1 See Section 1.0 of Method 7000.

2.0 SUMMARY OF METHOD

2.1 See Section 2.0 of Method 7000.

3.0 INTERFERENCES

3.1 If interferences are suspected, see Section 3.0 of Method 7000.

3.2 Background correction may be required since nonspecific absorption and scattering can be significant at the analytical wavelength. Background correction with certain instruments may be difficult at this wavelength due to low intensity output from hydrogen or deuterium lamps. Consult specific instrument manufacturer's literature for details.

4.0 APPARATUS AND MATERIALS

4.1 For basic apparatus, see Section 4.0 of Method 7000.

4.2 Instrument parameters (general):

4.2.1 Drying time and temp: 30 sec at 125°C.

4.2.2 Ashing time and temp: 30 sec at 900°C.

4.2.3 Atomizing time and temp: 10 sec at 2700°C.

4.2.4 Purge gas: Argon or nitrogen.

4.2.5 Wavelength: 324.7 nm.

4.2.6 Background correction: Recommended.

4.2.7 Other operating parameters should be set as specified by the particular instrument manufacturer.

NOTE: The above concentration values and instrument conditions are for a Perkin-Elmer HGA-2100, based on the use of a 20-uL injection, continuous-flow purge gas, and nonpyrolytic graphite. Smaller size furnace devices or those employing faster rates of atomization can be operated using lower atomization temperatures for shorter time periods than the above-recommended settings.

5.0 REAGENTS

5.1 See Section 5.0 of Method 7000.

5.2 Preparation of standards

5.2.1 Stock solution - Dissolve 1.00 g of electrolytic copper (analytical regent grade) in 5 mL redistilled HNO_3 and dilute to 1 liter with water. Alternatively, procure a certified standard from a supplier and verify by comparison with a second standard.

5.2.2 Prepare dilutions of the stock solution to be used as calibration standards at the time of analysis. The calibration standards should be prepared using the same type of acid and at the same concentrations as in the sample to be analyzed after processing (0.5% v/v HNO_3).

6.0 SAMPLE COLLECTION, PRESERVATION, AND HANDLING

6.1 See Chapter Three, Step 3.1.3, Sample Handling and Preservation.

7.0 PROCEDURE

7.1 Sample Preparation - The procedures for preparation of the sample are given in Chapter Three, Step 3.2.

7.2 See Method 7000, Step 7.3, Furnace Technique.

8.0 QUALITY CONTROL

8.1 See Section 8.0 of Method 7000.

9.0 METHOD PERFORMANCE

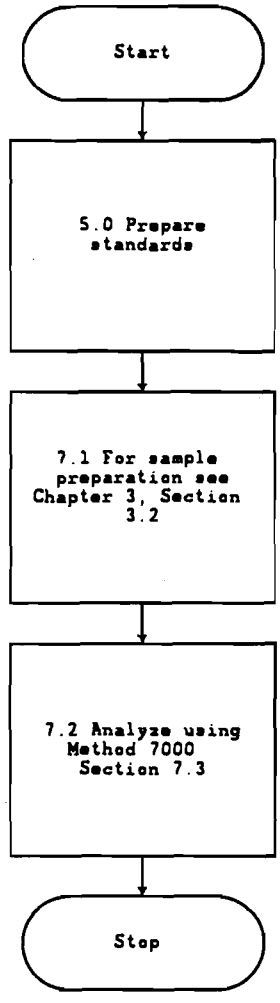
9.1 Precision and accuracy data are not available at this time.

9.2 The performance characteristics for an aqueous sample free of interferences are:

Optimum concentration range: 5-100 ug/L.
Detection limit: 1 ug/L.

10.0 REFERENCES

1. Methods for Chemical Analysis of Water and Wastes; U.S. Environmental Protection Agency. Office of Research and Development. Environmental Monitoring and Support Laboratory. ORD Publication Offices of Center for Environmental Research Information: Cincinnati, OH, 1983; EPA-600/4-79-020.


Start
5.0 Prepare standards
7.1 For sample preparation see Chapter 3, Section 3.2
7.2 Analyze using Method 7000 Section 7.3
Stop

METHOD 7380

IRON (ATOMIC ABSORPTION, DIRECT ASPIRATION)

1.0 SCOPE AND APPLICATION

1.1 See Section 1.0 of Method 7000.

2.0 SUMMARY OF METHOD

2.1 See Section 2.0 of Method 7000.

3.0 INTERFERENCES

3.1 See Section 3.0 of Method 7000 if interferences are suspected.

3.2 Iron is a universal contaminant, and great care should be taken to avoid contamination.

4.0 APPARATUS AND MATERIALS

4.1 For basic apparatus, see Section 4.0 of Method 7000.

4.2 Instrument parameters (general):

4.2.1 **Iron hollow cathode lamp.**
4.2.2 **Wavelength:** 248.3 nm (primary); 248.8, 271.9, 302.1, 252.7, or 372.0 nm (alternates).
4.2.3 **Fuel:** Acetylene.
4.2.4 **Oxidant:** Air.
4.2.5 **Type of flame:** Oxidizing (fuel lean).
4.2.6 **Background correction:** Required.

5.0 REAGENTS

5.1 See Section 5.0 of Method 7000.

5.2 Preparation of standards:

5.2.1 **Stock solution:** Dissolve 1.000 g iron wire (analytical reagent grade) in 10 mL redistilled HNO_3 and Type II water and dilute to 1 liter with Type II water. Note that iron passivates in concentrated HNO_3, and thus some water should be present. Alternatively, procure a certified standard from a supplier and verify by comparison with a second standard.

5.2.2 Prepare dilutions of the stock solution to be used as calibration standards at the time of analysis. The calibration standards should be prepared using the same type of acid and at the same concentration as will result in the sample to be analyzed after processing.

6.0 SAMPLE COLLECTION, PRESERVATION, AND HANDLING

6.1 See Chapter Three, Section 3.1.3, Sample Handling and Preservation.

7.0 PROCEDURE

7.1 Sample preparation: The procedures for preparation of the sample are given in Chapter Three, Section 3.2.

7.2 See Method 7000, Paragraph 7.2, Direct Aspiration.

8.0 QUALITY CONTROL

8.1 See Section 8.0 of Method 7000.

9.0 METHOD PERFORMANCE

9.1 The performance characteristics for an aqueous sample free of interferences are:

Optimum concentration range: 0.3-5 mg/L with a wavelength of 248.3 nm.
Sensitivity: 0.12 mg/L.
Detection limit: 0.03 mg/L.

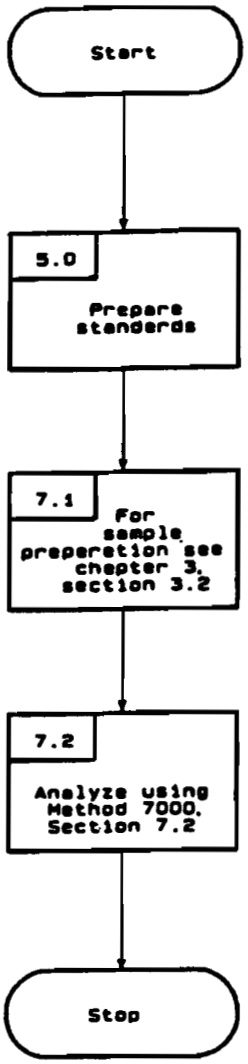
9.2 Precision and accuracy data are available in Method 236.1 of Methods for Chemical Analysis of Water and Wastes.

10.0 REFERENCES

1. Methods for Chemical Analysis of Water and Wastes, EPA-600/4-82-055, December 1982, Method 236.1.

METHOD 7380

IRON (ATOMIC ABSORPTION, DIRECT ASPIRATION)



METHOD 7381

IRON (ATOMIC ABSORPTION, FURNACE TECHNIQUE)

1.0 SCOPE AND APPLICATION

1.1 See Section 1.0 of Method 7000.

2.0 SUMMARY OF METHOD

2.1 See Section 2.0 of Method 7000.

3.0 INTERFERENCES

3.1 See Section 3.0 of Method 7000.

3.2 Iron is a universal contaminant, particularly at the low levels determined by this method. Great care should be taken to avoid contamination.

4.0 APPARATUS AND MATERIALS

4.1 For basic apparatus, see Section 4.0 of Method 7000.

4.2 Instrument parameters (general):

4.2.1 Drying time and temp: 30 sec at 125°C.

4.2.2 Ashing time and temp: 30 sec at 1000°C.

4.2.3 Atomizing time and temp: 10 sec at 2700°C.

4.2.4 Purge gas: Argon or nitrogen.

4.2.5 Wavelength: 248.3 nm.

4.2.6 Background Correction: Recommended.

4.2.7 Other operating parameters should be set as specified by the particular instrument manufacturer.

NOTE: The above concentration values and instrument conditions are for a Perkin-Elmer HGA-2100, based on the use of a 20-uL injection, continuous-flow purge gas, and nonpyrolytic graphite. Smaller size furnace devices or those employing faster rates of atomization can be operated using lower atomization temperatures for shorter time periods than the above-recommended settings.

5.0 REAGENTS

5.1 See Section 5.0 of Method 7000.

5.2 Preparation of standards

5.2.1 Stock solution - Dissolve 1.000 g iron wire (analytical reagent grade) in 10 mL redistilled HNO_3 and water and dilute to 1 liter with water. Note that iron passivates in concentrated HNO_3 and, thus, some water should be present. Alternatively, procure a certified standard from a supplier and verify by comparison with a second standard.

5.2.2 Prepare dilutions of the stock solution to be used as calibration standards at the time of analysis. The calibration standards should be prepared using the same type of acid and at the same concentrations as in the sample to be analyzed after processing (0.5% v/v HNO_3).

6.0 SAMPLE COLLECTION, PRESERVATION AND HANDLING

6.1 See Chapter Three, Step 3.1.3, Sample Handling and Preservation.

7.0 PROCEDURE

7.1 Sample preparation - The procedures for preparation of the sample are given in Chapter Three, Step 3.2.

7.2 See Method 7000, Step 7.3, Furnace Technique.

8.0 QUALITY CONTROL

8.1 See Section 8.0 of Method 7000.

9.0 METHOD PERFORMANCE

9.1 Precision and accuracy data are not available at this time.

9.2 The performance characteristics for an aqueous sample free of interferences are:

Optimum concentration range: 5-100 ug/L.
Detection limit: 1 ug/L.

10.0 REFERENCES

1. Methods for Chemical Analysis of Water and Wastes; U.S. Environmental Protection Agency. Office of Research and Development. Environmental Monitoring and Support Laboratory. ORD Publication Offices of Center for Environmental Research Information: Cincinnati, OH, 1983; EPA-600/4-79-020.

METHOD 7460

MANGANESE (ATOMIC ABSORPTION, DIRECT ASPIRATION)

1.0 SCOPE AND APPLICATION

1.1 See Section 1.0 of Method 7000.

2.0 SUMMARY OF METHOD

2.1 See Section 2.0 of Method 7000.

3.0 INTERFERENCES

3.1 See Section 3.0 of Method 7000 if interferences are suspected.

3.2 Background correction is required.

4.0 APPARATUS AND MATERIALS

4.1 For basic apparatus, see Section 4.0 of Method 7000.

4.2 Instrument parameters (general):

4.2.1 **Manganese hollow cathode lamp.**
4.2.2 **Wavelength:** 279.5 nm (primary); 403.1 nm (alternate).
4.2.3 **Fuel:** Acetylene.
4.2.4 **Oxidant:** Air.
4.2.5 **Type of flame:** Slightly oxidizing (slightly fuel-lean to stoichiometric).
4.2.6 **Background correction:** Required.

5.0 REAGENTS

5.1 See Section 5.0 of Method 7000.

5.2 Preparation of standards:

5.2.1 **Stock solution:** Dissolve 1.000 g manganese metal (analytical reagent grade) in 10 mL redistilled HNO_3 and dilute to 1 liter with Type II water. Alternatively, procure a certified standard from a supplier and verify by comparison with a second standard.

5.2.2 Prepare dilutions of the stock solution to be used as calibration standards at the time of analysis. The calibration standards should be prepared using the same type of acid and at the same concentration as will result in the sample to be analyzed after processing.

6.0 SAMPLE COLLECTION, PRESERVATION, AND HANDLING

6.1 See Chapter Three, Section 3.1.3, Sample Handling and Preservation.

7.0 PROCEDURE

7.1 Sample preparation: The procedures for preparation of the sample are given in Chapter Three, Section 3.2.

7.2 See Method 7000, Paragraph 7.2, Direct Aspiration.

8.0 QUALITY CONTROL

8.1 See Section 8.0 of Method 7000.

9.0 METHOD PERFORMANCE

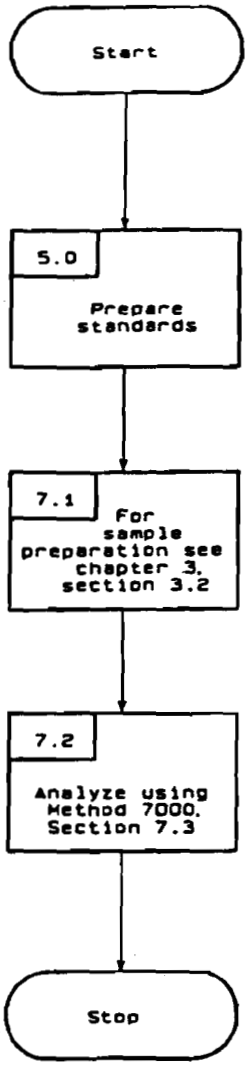
9.1 The performance characteristics for an aqueous sample free of interferences are:

Optimum concentration range: 0.1-3 mg/L with a wavelength of 279.5 nm.
Sensitivity: 0.05 mg/L.
Detection limit: 0.01 mg/L.

9.2 Precision and accuracy data are available in Method 243.1 of Methods for Chemical Analysis of Water and Wastes.

10.0 REFERENCES

1. Methods for Chemical Analysis of Water and Wastes, EPA-600/4-82-055, December 1982, Method 243.1.


Start
5.0
Prepare standards
7.1
For sample preparation see chapter 3, section 3.2
7.2
Analyze using Method 7000, Section 7.3
Stop

METHOD 7470A

MERCURY IN LIQUID WASTE (MANUAL COLD-VAPOR TECHNIQUE)

1.0 SCOPE AND APPLICATION

1.1 Method 7470 is a cold-vapor atomic absorption procedure approved for determining the concentration of mercury in mobility-procedure extracts, aqueous wastes, and ground waters. (Method 7470 can also be used for analyzing certain solid and sludge-type wastes; however, Method 7471 is usually the method of choice for these waste types.) All samples must be subjected to an appropriate dissolution step prior to analysis.

2.0 SUMMARY OF METHOD

2.1 Prior to analysis, the liquid samples must be prepared according to the procedure discussed in this method.

2.2 Method 7470, a cold-vapor atomic absorption technique, is based on the absorption of radiation at 253.7-nm by mercury vapor. The mercury is reduced to the elemental state and aerated from solution in a closed system. The mercury vapor passes through a cell positioned in the light path of an atomic absorption spectrophotometer. Absorbance (peak height) is measured as a function of mercury concentration.

2.3 The typical detection limit for this method is 0.0002 mg/L.

3.0 INTERFERENCES

3.1 Potassium permanganate is added to eliminate possible interference from sulfide. Concentrations as high as 20 mg/L of sulfide as sodium sulfide do not interfere with the recovery of added inorganic mercury from reagent water.

3.2 Copper has also been reported to interfere; however, copper concentrations as high as 10 mg/L had no effect on recovery of mercury from spiked samples.

3.3 Seawaters, brines, and industrial effluents high in chlorides require additional permanganate (as much as 25 mL) because, during the oxidation step, chlorides are converted to free chlorine, which also absorbs radiation of 253.7 nm. Care must therefore be taken to ensure that free chlorine is absent before the mercury is reduced and swept into the cell. This may be accomplished by using an excess of hydroxylamine sulfate reagent (25 mL). In addition, the dead air space in the BOD bottle must be purged before adding stannous sulfate. Both inorganic and organic mercury spikes have been quantitatively recovered from seawater by using this technique.

3.4 Certain volatile organic materials that absorb at this wavelength may also cause interference. A preliminary run without reagents should determine if this type of interference is present.

4.0 APPARATUS AND MATERIALS

4.1 Atomic absorption spectrophotometer or equivalent: Any atomic absorption unit with an open sample presentation area in which to mount the absorption cell is suitable. Instrument settings recommended by the particular manufacturer should be followed. Instruments designed specifically for the measurement of mercury using the cold-vapor technique are commercially available and may be substituted for the atomic absorption spectrophotometer.

4.2 Mercury hollow cathode lamp or electrodeless discharge lamp.

4.3 Recorder: Any multirange variable-speed recorder that is compatible with the UV detection system is suitable.

4.4 Absorption cell: Standard spectrophotometer cells 10 cm long with quartz end windows may be used. Suitable cells may be constructed from Plexiglas tubing, 1 in. O.D. x 4.5 in. The ends are ground perpendicular to the longitudinal axis, and quartz windows (1 in. diameter x 1/16 in. thickness) are cemented in place. The cell is strapped to a burner for support and aligned in the light beam by use of two 2-in. x 2-in. cards. One-in.-diameter holes are cut in the middle of each card. The cards are then placed over each end of the cell. The cell is then positioned and adjusted vertically and horizontally to give the maximum transmittance.

4.5 Air pump: Any peristaltic pump capable of delivering 1 liter air/min may be used. A Masterflex pump with electronic speed control has been found to be satisfactory.

4.6 Flowmeter: Capable of measuring an air flow of 1 liter/min.

4.7 Aeration tubing: A straight glass frit with a coarse porosity. Tygon tubing is used for passage of the mercury vapor from the sample bottle to the absorption cell and return.

4.8 Drying tube: 6-in. x 3/4-in.-diameter tube containing 20 g of magnesium perchlorate or a small reading lamp with 60-W bulb which may be used to prevent condensation of moisture inside the cell. The lamp should be positioned to shine on the absorption cell so that the air temperature in the cell is about 10°C above ambient.

4.9 The cold-vapor generator is assembled as shown in Figure 1 of reference 1 or according to the instrument manufacturers instructions. The apparatus shown in Figure 1 is a closed system. An open system, where the mercury vapor is passed through the absorption cell only once, may be used instead of the closed system. Because mercury vapor is toxic, precaution must be taken to avoid its inhalation. Therefore, a bypass has been included in the system either to vent the mercury vapor into an exhaust hood or to pass the vapor through some absorbing medium, such as:

1. Equal volumes of 0.1 M $KMnO_4$ and 10% H_2SO_4; or

2. 0.25% Iodine in a 3% KI solution.

A specially treated charcoal that will adsorb mercury vapor is also available from Barnebey and Cheney, East 8th Avenue and North Cassidy Street, Columbus, Ohio 43219, Cat. #580-13 or #580-22.

4.10 Hot plate or equivalent - Adjustable and capable of maintaining a temperature of 90-95°C.

4.11 Graduated cylinder or equivalent.

5.0 REAGENTS

5.1 Reagent Water: Reagent water will be interference free. All references to water in this method will refer to reagent water unless otherwise specified.

5.2 Sulfuric acid (H_2SO_4), concentrated: Reagent grade.

5.3 Sulfuric acid, 0.5 N: Dilute 14.0 mL of concentrated sulfuric acid to 1.0 liter.

5.4 Nitric acid (HNO_3), concentrated: Reagent grade of low mercury content. If a high reagent blank is obtained, it may be necessary to distill the nitric acid.

5.5 Stannous sulfate: Add 25 g stannous sulfate to 250 mL of 0.5 N H_2SO_4. This mixture is a suspension and should be stirred continuously during use. (Stannous chloride may be used in place of stannous sulfate.)

5.6 Sodium chloride-hydroxylamine sulfate solution: Dissolve 12 g of sodium chloride and 12 g of hydroxylamine sulfate in reagent water and dilute to 100 mL. (Hydroxylamine hydrochloride may be used in place of hydroxylamine sulfate.)

5.7 Potassium permanganate, mercury-free, 5% solution (w/v): Dissolve 5 g of potassium permanganate in 100 mL of reagent water.

5.8 Potassium persulfate, 5% solution (w/v): Dissolve 5 g of potassium persulfate in 100 mL of reagent water.

5.9 Stock mercury solution: Dissolve 0.1354 g of mercuric chloride in 75 mL of reagent water. Add 10 mL of concentrated HNO_3 and adjust the volume to 100.0 mL (1 mL = 1 mg Hg). Stock solutions may also be purchased.

5.10 Mercury working standard: Make successive dilutions of the stock mercury solution to obtain a working standard containing 0.1 ug per mL. This working standard and the dilutions of the stock mercury solution should be prepared fresh daily. Acidity of the working standard should be maintained at 0.15% nitric acid. This acid should be added to the flask, as needed, before addition of the aliquot.

6.0 SAMPLE COLLECTION, PRESERVATION, AND HANDLING

6.1 All samples must have been collected using a sampling plan that addresses the considerations discussed in Chapter Nine of this manual.

6.2 All sample containers must be prewashed with detergents, acids, and reagent water. Plastic and glass containers are both suitable.

6.3 Aqueous samples must be acidified to a pH <2 with HNO_3. The suggested maximum holding times for mercury is 28 days.

6.4 Nonaqueous samples shall be refrigerated, when possible, and analyzed as soon as possible.

7.0 PROCEDURE

7.1 Sample preparation: Transfer 100 mL, or an aliquot diluted to 100 mL, containing <1.0 g of mercury, to a 300-mL BOD bottle or equivalent. Add 5 mL of H_2SO_4 and 2.5 mL of concentrated HNO_3, mixing after each addition. Add 15 mL of potassium permanganate solution to each sample bottle. Sewage samples may require additional permanganate. Ensure that equal amounts of permanganate are added to standards and blanks. Shake and add additional portions of potassium permanganate solution, if necessary, until the purple color persists for at least 15 min. Add 8 mL of potassium persulfate to each bottle and heat for 2 hr in a water bath maintained at 95°C. Cool and add 6 mL of sodium chloride-hydroxylamine sulfate to reduce the excess permanganate. After a delay of at least 30 sec, add 5 mL of stannous sulfate, immediately attach the bottle to the aeration apparatus, and continue as described in Paragraph 7.3.

7.2 Standard preparation: Transfer 0-, 0.5-, 1.0-, 2.0-, 5.0-, and 10.0-mL aliquots of the mercury working standard, containing 0-1.0 ug of mercury, to a series of 300-mL BOD bottles. Add enough reagent water to each bottle to make a total volume of 100 mL. Mix thoroughly and add 5 mL of concentrated H_2SO_4 and 2.5 mL of concentrated HNO_3 to each bottle. Add 15 mL of $KMnO_4$ solution to each bottle and allow to stand at least 15 min. Add 8 mL of potassium persulfate to each bottle and heat for 2 hr in a water bath maintained at 95°C. Cool and add 6 mL of sodium chloride-hydroxylamine sulfate solution to reduce the excess permanganate. When the solution has been decolorized, wait 30 sec, add 5 mL of the stannous sulfate solution, immediately attach the bottle to the aeration apparatus, and continue as described in Paragraph 7.3.

7.3 Analysis: At this point the sample is allowed to stand quietly without manual agitation. The circulating pump, which has previously been adjusted to a rate of 1 liter/min, is allowed to run continuously. The absorbance will increase and reach a maximum within 30 sec. As soon as the recorder pen levels off (approximately 1 min), open the bypass valve and continue the aeration until the absorbance returns to its minimum value. Close the bypass valve, remove the stopper and frit from the BOD bottle, and continue the aeration. Because of instrument variation refer to the manufacturers recommended operating conditions when using this method.

7.4 Construct a calibration curve by plotting the absorbances of standards versus micrograms of mercury. Determine the peak height of the unknown from the chart and read the mercury value from the standard curve. Duplicates, spiked samples, and check standards should be routinely analyzed.

7.5 Calculate metal concentrations (1) by the method of standard additions, or (2) from a calibration curve. All dilution or concentration factors must be taken into account. Concentrations reported for multiphased or wet samples must be appropriately qualified (e.g., 5 ug/g dry weight).

8.0 QUALITY CONTROL

8.1 Refer to section 8.0 of Method 7000.

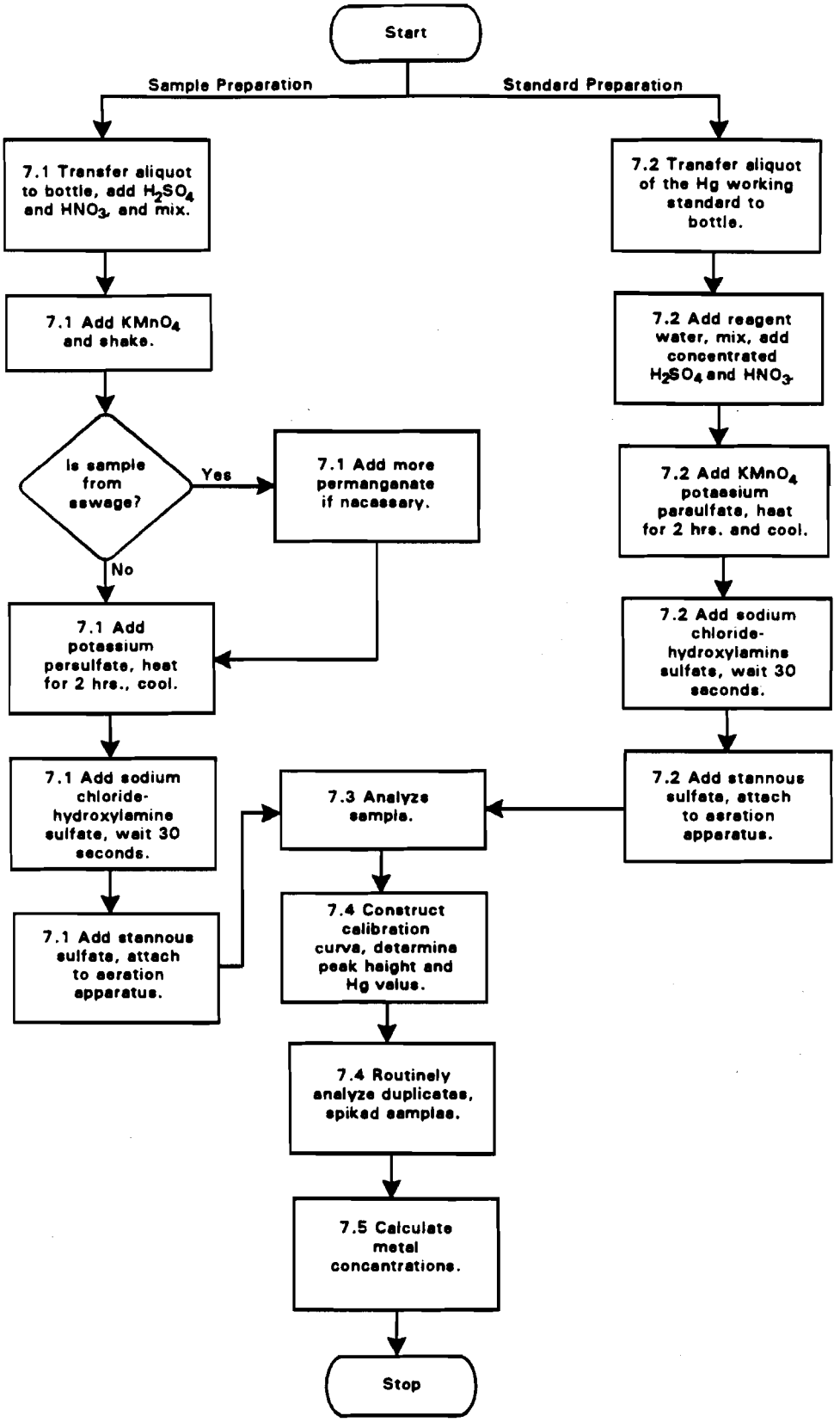
9.0 METHOD PERFORMANCE

9.1 Precision and accuracy data are available in Method 245.1 of Methods for Chemical Analysis of Water and Wastes.

10.0 REFERENCES

1. Methods for Chemical Analysis of Water and Wastes, EPA-600/4-82-055, December 1982, Method 245.1.

METHOD 7470A
MERCURY IN LIQUID WASTE (MANUAL COLD-VAPOR TECHNIQUE)



METHOD 7471A

MERCURY IN SOLID OR SEMISOLID WASTE (MANUAL COLD-VAPOR TECHNIQUE)

1.0 SCOPE AND APPLICATION

1.1 Method 7471 is approved for measuring total mercury (organic and inorganic) in soils, sediments, bottom deposits, and sludge-type materials. All samples must be subjected to an appropriate dissolution step prior to analysis. If this dissolution procedure is not sufficient to dissolve a specific matrix type or sample, then this method is not applicable for that matrix.

2.0 SUMMARY OF METHOD

2.1 Prior to analysis, the solid or semi-solid samples must be prepared according to the procedures discussed in this method.

2.2 Method 7471, a cold-vapor atomic absorption method, is based on the absorption of radiation at the 253.7-nm wavelength by mercury vapor. The mercury is reduced to the elemental state and aerated from solution in a closed system. The mercury vapor passes through a cell positioned in the light path of an atomic absorption spectrophotometer. Absorbance (peak height) is measured as a function of mercury concentration.

2.3 The typical instrument detection limit (IDL) for this method is 0.0002 mg/L.

3.0 INTERFERENCES

3.1 Potassium permanganate is added to eliminate possible interference from sulfide. Concentrations as high as 20 mg/Kg of sulfide, as sodium sulfide, do not interfere with the recovery of added inorganic mercury in reagent water.

3.2 Copper has also been reported to interfere; however, copper concentrations as high as 10 mg/Kg had no effect on recovery of mercury from spiked samples.

3.3 Samples high in chlorides require additional permanganate (as much as 25 mL) because, during the oxidation step, chlorides are converted to free chlorine, which also absorbs radiation of 253 nm. Care must therefore be taken to ensure that free chlorine is absent before the mercury is reduced and swept into the cell. This may be accomplished by using an excess of hydroxylamine sulfate reagent (25 mL). In addition, the dead air space in the BOD bottle must be purged before adding stannous sulfate.

3.4 Certain volatile organic materials that absorb at this wavelength may also cause interference. A preliminary run without reagents should determine if this type of interference is present.

4.0 APPARATUS AND MATERIALS

4.1 Atomic absorption spectrophotometer or equivalent: Any atomic absorption unit with an open sample presentation area in which to mount the

absorption cell is suitable. Instrument settings recommended by the particular manufacturer should be followed. Instruments designed specifically for the measurement of mercury using the cold-vapor technique are commercially available and may be substituted for the atomic absorption spectrophotometer.

4.2 Mercury hollow cathode lamp or electrodeless discharge lamp.

4.3 Recorder: Any multirange variable-speed recorder that is compatible with the UV detection system is suitable.

4.4 Absorption cell: Standard spectrophotometer cells 10 cm long with quartz end windows may be used. Suitable cells may be constructed from Plexiglas tubing, 1 in. O.D. x 4.5 in. The ends are ground perpendicular to the longitudinal axis, and quartz windows (1 in. diameter x 1/16 in. thickness) are cemented in place. The cell is strapped to a burner for support and aligned in the light beam by use of two 2-in. x 2-in. cards. One-in.-diameter holes are cut in the middle of each card. The cards are then placed over each end of the cell. The cell is then positioned and adjusted vertically and horizontally to give the maximum transmittance.

4.5 Air pump: Any peristaltic pump capable of delivering 1 L/min air may be used. A Masterflex pump with electronic speed control has been found to be satisfactory.

4.6 Flowmeter: Capable of measuring an air flow of 1 L/min.

4.7 Aeration tubing: A straight glass frit with a coarse porosity. Tygon tubing is used for passage of the mercury vapor from the sample bottle to the absorption cell and return.

4.8 Drying tube: 6-in. x 3/4-in.-diameter tube containing 20 g of magnesium perchlorate or a small reading lamp with 60-W bulb which may be used to prevent condensation of moisture inside the cell. The lamp should be positioned to shine on the absorption cell so that the air temperature in the cell is about 10°C above ambient.

4.9 The cold-vapor generator is assembled as shown in Figure 1 of reference 1 or according to the instrument manufacturers instructions. The apparatus shown in Figure 1 is a closed system. An open system, where the mercury vapor is passed through the absorption cell only once, may be used instead of the closed system. Because mercury vapor is toxic, precaution must be taken to avoid its inhalation. Therefore, a bypass has been included in the system either to vent the mercury vapor into an exhaust hood or to pass the vapor through some absorbing medium, such as:

1. equal volumes of 0.1 M $KMnO_4$ and 10% H_2SO_4, or
2. 0.25% iodine in a 3% KI solution.

A specially treated charcoal that will adsorb mercury vapor is also available from Barneby and Cheney, East 8th Avenue and North Cassidy Street, Columbus, Ohio 43219, Cat. #580-13 or #580-22.

4.10 Hot plate or equivalent - Adjustable and capable of maintaining a temperature of 90-95°C.

4.11 Graduated cylinder or equivalent.

5.0 REAGENTS

5.1 Reagent Water: Reagent water will be interference free. All references to water in this method refer to reagent water unless otherwise specified.

5.2 Aqua regia: Prepare immediately before use by carefully adding three volumes of concentrated HCl to one volume of concentrated HNO_3.

5.3 Sulfuric acid, 0.5 N: Dilute 14.0 mL of concentrated sulfuric acid to 1 liter.

5.4 Stannous sulfate: Add 25 g stannous sulfate to 250 mL of 0.5 N sulfuric acid. This mixture is a suspension and should be stirred continuously during use. A 10% solution of stannous chloride can be substituted for stannous sulfate.

5.5 Sodium chloride-hydroxylamine sulfate solution: Dissolve 12 g of sodium chloride and 12 g of hydroxylamine sulfate in reagent water and dilute to 100 mL. Hydroxylamine hydrochloride may be used in place of hydroxylamine sulfate.

5.6 Potassium permanganate, mercury-free, 5% solution (w/v): Dissolve 5 g of potassium permanganate in 100 mL of reagent water.

5.7 Mercury stock solution: Dissolve 0.1354 g of mercuric chloride in 75 mL of reagent water. Add 10 mL of concentrated nitric acid and adjust the volume to 100.0 mL (1.0 mL = 1.0 mg Hg).

5.8 Mercury working standard: Make successive dilutions of the stock mercury solution to obtain a working standard containing 0.1 ug/mL. This working standard and the dilution of the stock mercury solutions should be prepared fresh daily. Acidity of the working standard should be maintained at 0.15% nitric acid. This acid should be added to the flask, as needed, before adding the aliquot.

6.0 SAMPLE COLLECTION, PRESERVATION, AND HANDLING

6.1 All samples must have been collected using a sampling plan that addresses the considerations discussed in Chapter Nine of this manual.

6.2 All sample containers must be prewashed with detergents, acids, and reagent water. Plastic and glass containers are both suitable.

6.3 Non-aqueous samples shall be refrigerated, when possible, and analyzed as soon as possible."

7.0 PROCEDURE

7.1 Sample preparation: Weigh triplicate 0.2-g portions of untreated sample and place in the bottom of a BOD bottle. Add 5 mL of reagent water and 5 mL of aqua regia. Heat 2 min in a water bath at 95°C. Cool; then add 50 mL reagent water and 15 mL potassium permanganate solution to each sample bottle. Mix thoroughly and place in the water bath for 30 min at 95°C. Cool and add 6 mL of sodium chloride-hydroxylamine sulfate to reduce the excess permanganate.

> CAUTION: Do this addition under a hood, as Cl_2 could be evolved. Add 55 mL of reagent water. Treating each bottle individually, add 5 mL of stannous sulfate and immediately attach the bottle to the aeration apparatus. Continue as described under step 7.4.

7.2 An alternate digestion procedure employing an autoclave may also be used. In this method, 5 mL of concentrated H_2SO_4 and 2 mL of concentrated HNO_3 are added to the 0.2 g of sample. Add 5 mL of saturated $KMnO_4$ solution and cover the bottle with a piece of aluminum foil. The samples are autoclaved at 121°C and 15 lb for 15 min. Cool, dilute to a volume of 100 mL with reagent water, and add 6 mL of sodium chloride-hydroxylamine sulfate solution to reduce the excess permanganate. Purge the dead air space and continue as described under step 7.4. Refer to the caution statement in section 7.1 for the proper protocol in reducing the excess permanganate solution and adding stannous sulfate.

7.3 Standard preparation: Transfer 0.0-, 0.5-, 1.0-, 2.0-, 5.0-, and 10-mL aliquots of the mercury working standard, containing 0-1.0 ug of mercury, to a series of 300-mL BOD bottles or equivalent. Add enough reagent water to each bottle to make a total volume of 10 mL. Add 5 mL of aqua regia and heat 2 min in a water bath at 95°C. Allow the sample to cool; add 50 mL reagent water and 15 mL of $KMnO_4$ solution to each bottle and return to the water bath for 30 min. Cool and add 6 mL of sodium chloride-hydroxylamine sulfate solution to reduce the excess permanganate. Add 50 mL of reagent water. Treating each bottle individually, add 5 mL of stannous sulfate solution, immediately attach the bottle to the aeration apparatus, and continue as described in Step 7.4.

7.4 Analysis: At this point, the sample is allowed to stand quietly without manual agitation. The circulating pump, which has previously been adjusted to a rate of 1 L/min, is allowed to run continuously. The absorbance, as exhibited either on the spectrophotometer or the recorder, will increase and reach maximum within 30 sec. As soon as the recorder pen levels off (approximately 1 min), open the bypass valve and continue the aeration until the absorbance returns to its minimum value. Close the bypass valve, remove the fritted tubing from the BOD bottle, and continue the aeration.

7.5 Construct a calibration curve by plotting the absorbances of standards versus micrograms of mercury. Determine the peak height of the unknown from the chart and read the mercury value from the standard curve. Duplicates, spiked samples, and check standards should be routinely analyzed.

7.6 Calculate metal concentrations: (1) by the method of standard additions, (2) from a calibration curve, or (3) directly from the instrument's concentration read-out. All dilution or concentration factors must be taken into

account. Concentrations reported for multiphased or wet samples must be appropriately qualified (e.g., 5 ug/g dry weight).

8.0 QUALITY CONTROL

8.1 Refer to section 8.0 of Method 7000.

9.0 METHOD PERFORMANCE

9.1 Precision and accuracy data are available in Method 245.5 of Methods for Chemical Analysis of Water and Wastes.

9.2 The data shown in Table 1 were obtained from records of state and contractor laboratories. The data are intended to show the precision of the combined sample preparation and analysis method.

10.0 REFERENCES

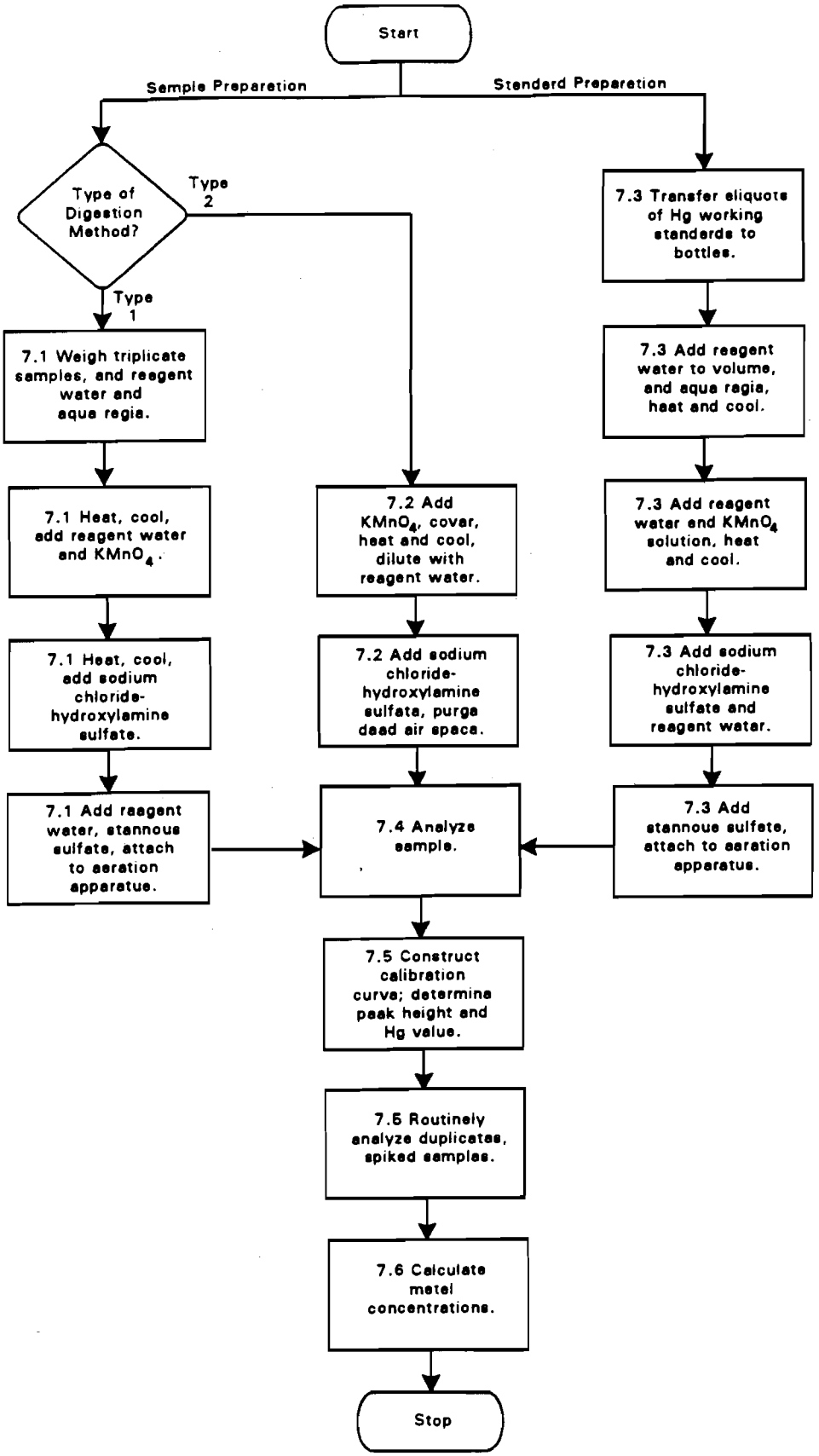
1. Methods for Chemical Analysis of Water and Wastes, EPA-600/4-82-055, December 1982, Method 245.5.

2. Gaskill, A., Compilation and Evaluation of RCRA Method Performance Data, Work Assignment No. 2, EPA Contract No. 68-01-7075, September 1986.

TABLE 1. METHOD PERFORMANCE DATA

Sample Matrix	Preparation Method	Laboratory Replicates
Emission control dust	Not known	12, 12 ug/g
Wastewater treatment sludge	Not known	0.4, 0.28 ug/g

METHOD 7471A
MERCURY IN SOLID OR SEMISOLID WASTE (MANUAL COLD-VAPOR TECHNIQUE)



Revision 1
September 1994

METHOD 7480

MOLYBDENUM (ATOMIC ABSORPTION, DIRECT ASPIRATION)

1.0 SCOPE AND APPLICATION

1.1 See Section 1.0 of Method 7000.

2.0 SUMMARY OF METHOD

2.1 See Section 2.0 of Method 7000.

3.0 INTERFERENCES

3.1 See Section 3.0 of Method 7000 if interferences are suspected.

3.2 Interferences in an air/acetylene flame from Ca, Sr, SO_4, and Fe are severe. These interferences are greatly reduced in the nitrous oxide flame and by addition of 1,000 mg/L aluminum to samples and standards.

4.0 APPARATUS AND MATERIALS

4.1 For basic apparatus, see Section 4.0 of Method 7000.

4.2 Instrument parameters (general):

4.2.1 **Molybdenum hollow cathode lamp.**
4.2.2 **Wavelength:** 313.3 nm.
4.2.3 **Fuel:** Acetylene.
4.2.4 **Oxidant:** Nitrous oxide.
4.2.5 **Type of flame:** Fuel rich.
4.2.6 **Background correction:** Required.

5.0 REAGENTS

5.1 See Section 5.0 of Method 7000.

5.2 Preparation of standards:

5.2.1 **Stock solution:** Dissolve 1.840 g of ammonium molybdate, $(NH_4)_6Mo_7O_{24}\cdot 4H_2O$ (analytical reagent grade), in Type II water and dilute to 1 liter; 1 mL = 1 mg Mo (1,000 mg/L). Alternatively, procure a certified standard from a supplier and verify by comparison with a second standard.

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5.2.2 Prepare dilutions of the stock solution to be used as calibration standards at the time of analysis. The calibration standards should be prepared using the same type of acid and at the same concentration as will result in the sample to be analyzed after processing. The samples and standards should also contain 1,000 mg/L aluminum (see Paragraph 5.2.3).

5.2.3 **Aluminum nitrate solution:** Dissolve 139 g aluminum nitrate, $Al(NO_3)_3 \cdot 9H_2O$, in 150 mL of Type II water; heat to effect solution. Allow to cool and make up to 200 mL. To each 100 mL of standard and sample alike, add 2 mL of the aluminum nitrate solution.

6.0 SAMPLE COLLECTION, PRESERVATION, AND HANDLING

6.1 See Chapter Three, Section 3.1.3, Sample Handling and Preservation.

7.0 PROCEDURE

7.1 Sample preparation: The procedures for preparation of the sample are given in Chapter Three, Section 3.2.

7.2 See Method 7000, Paragraph 7.2, Direct Aspiration.

8.0 QUALITY CONTROL

8.1 See Section 8.0 of Method 7000.

9.0 METHOD PERFORMANCE

9.1 The performance characteristics for an aqueous sample free of interferences are:

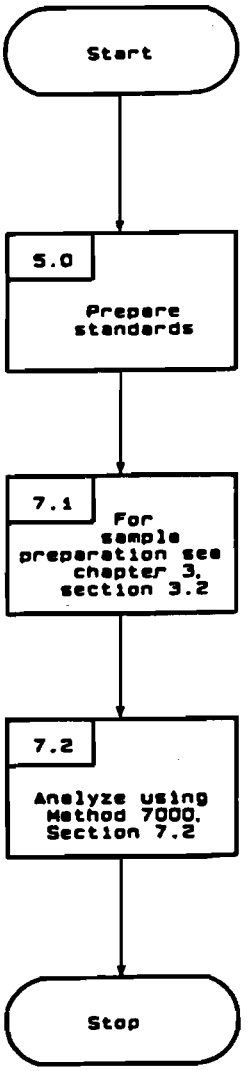
Optimum concentration range: 1-40 mg/L with a wavelength of 313.3 nm.
Sensitivity: 0.4 mg/L.
Detection limit: 0.1 mg/L.

9.2 In a single laboratory, analysis of a mixed industrial-domestic waste effluent, digested with Method 3010, at concentrations of 0.3, 1.5, and 7.5 mg/L gave standard deviations of ±0.007, ±0.02, and ±0.07, respectively. Recoveries at these levels were 100%, 96%, and 95%, respectively.

9.3 For concentrations of molybdenum below 0.2 mg/L, the furnace technique (Method 7481) is recommended.

10.0 REFERENCES

1. Methods for Chemical Analysis of Water and Wastes, EPA-600/4-82-055, December 1982, Method 246.1.


Start
5.0
Prepare standards
7.1
For sample preparation see chapter 3, section 3.2
7.2
Analyze using Method 7000, Section 7.2
Stop

METHOD 7481

MOLYBDENUM (ATOMIC ABSORPTION, FURNACE TECHNIQUE)

1.0 SCOPE AND APPLICATION

1.1 See Section 1.0 of Method 7000.

2.0 SUMMARY OF METHOD

2.1 See Section 2.0 of Method 7000.

3.0 INTERFERENCES

3.1 See Section 3.0 of Method 7000 if interferences are suspected.

3.2 Molybdenum is prone to carbide formation. Use a pyrolytically coated graphite tube.

3.3 Memory effects are possible, and cleaning of the furnace may be required after analysis of more concentrated samples or standards.

4.0 APPARATUS AND MATERIALS

4.1 For basic apparatus, see Section 4.0 of Method 7000.

4.2 Instrument parameters (general):

4.2.1 **Drying time and temp:** 30 sec at 125°C.
4.2.2 **Ashing time and temp:** 30 sec at 1400°C.
4.2.3 **Atomizing time and temp:** 5 sec at 2800°C.
4.2.4 **Purge gas:** Argon (nitrogen should not be used).
4.2.5 **Wavelength:** 313.3 nm.
4.2.6 **Background correction:** Required.
4.2.7 Other operating parameters should be set as specified by the particular instrument manufacturer.
4.2.8 **Pyrolytically coated graphite tube.**

NOTE: The above concentration values and instrument conditions are for a Perkin-Elmer HGA-2100, based on the use of a 20-uL injection, continuous-flow purge gas, and nonpyrolytic graphite. Smaller sizes of furnace devices or those employing faster rates of atomization can be operated using lower atomization temperatures for shorter time periods than the above-recommended settings.

5.0 REAGENTS

5.1 See Section 5.0 of Method 7000.

5.2 Preparation of standards:

5.2.1 Stock solution: Dissolve 1.840 g of ammonium molybdate, $(NH_4)_6Mo_7O_{24}\cdot 4H_2O$ (analytical reagent grade), in Type II water and dilute to 1 liter; 1 mL = 1 mg Mo (1,000 mg/L). Alternatively, procure a certified standard from a supplier and verify by comparison with a second standard.

5.2.2 Prepare dilutions of the stock solution to be used as calibration standards at the time of analysis. The calibration standards should be prepared using the same type of acid and at the same concentrations as in the sample after processing (0.5% v/v HNO_3).

6.0 SAMPLE COLLECTION, PRESERVATION, AND HANDLING

6.1 See Chapter Three, Section 3.1.3, Sample Handling and Preservation.

7.0 PROCEDURE

7.1 Sample preparation: The procedures for preparation of the sample are given in Chapter Three, Section 3.2.

7.2 See Method 7000, Paragraph 7.3, Furnace Procedure. The calculation is given in Method 7000, Paragraph 7.4.

8.0 QUALITY CONTROL

8.1 See Section 8.0 of Method 7000.

9.0 METHOD PERFORMANCE

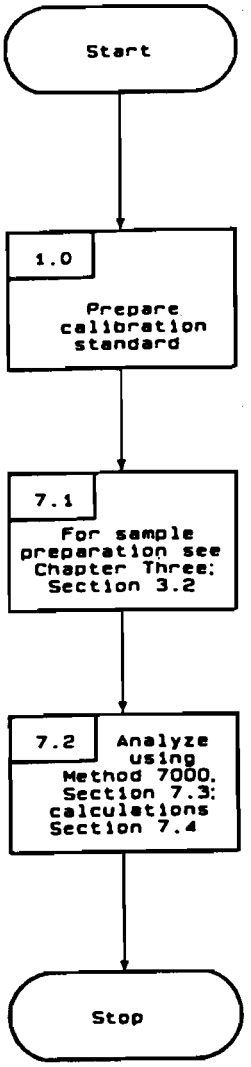
9.1 Precision and accuracy data are not available at this time.

9.2 The performance characteristics for an aqueous sample free of interferences are:

Optimum concentration range: 3-60 ug/L.
Detection limit: 1 ug/L.

10.0 REFERENCES

1. Methods for Chemical Analysis of Water and Wastes, EPA-600/4-82-055, December 1982, Method 246.2.


Start
1.0
Prepare calibration standard
7.1
For sample preparation see Chapter Three: Section 3.2
7.2
Analyze using Method 7000, Section 7.3; calculations Section 7.4
Stop

METHOD 7520

NICKEL (ATOMIC ABSORPTION, DIRECT ASPIRATION)

1.0 SCOPE AND APPLICATION

1.1 See Section 1.0 of Method 7000.

2.0 SUMMARY OF METHOD

2.1 See Section 2.0 of Method 7000.

3.0 INTERFERENCES

3.1 See Section 3.0 of Method 7000 if interferences are suspected.

3.2 Background correction is required.

3.3 High concentrations of iron, cobalt, or chromium may interfere, requiring either matrix matching or use of a nitrous-oxide/acetylene flame.

3.4 A nonresonance line of Ni at 232.14 nm causes nonlinear calibration curves at moderate to high nickel concentrations, requiring sample dilution or use of the 352.4-nm line.

4.0 APPARATUS AND MATERIALS

4.1 For basic apparatus, see Section 4.0 of Method 7000.

4.2 Instrument parameters (general):

4.2.1 **Nickel hollow cathode lamp.**
4.2.2 **Wavelength:** 232.0 nm (primary); 352.4 nm (alternate).
4.2.3 **Fuel:** Acetylene.
4.2.4 **Oxidant:** Air.
4.2.5 **Type of flame:** Oxidizing (fuel lean).
4.2.6 **Background correction:** Required.

5.0 REAGENTS

5.1 See Section 5.0 of Method 7000.

5.2 Preparation of standards:

5.2.1 **Stock solution:** Dissolve 1.000 g nickel metal (analytical reagent grade) or 4.953 g nickel nitrate, $Ni(NO_3)_2 \cdot 6H_2O$ (analytical reagent grade), in 10 mL HNO_3 and dilute to 1 liter with Type II water.

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Alternatively, procure a certified standard from a supplier and verify by comparison with a second standard.

5.2.2 Prepare dilutions of the stock solution to be used as calibration standards at the time of analysis. The calibration standards should be prepared using the same type of acid and at the same concentration as will result in the sample to be analyzed after processing.

6.0 SAMPLE COLLECTION, PRESERVATION, AND HANDLING

6.1 See Chapter Three, Section 3.1.3, Sample Handling and Preservation.

7.0 PROCEDURE

7.1 Sample preparation: The procedures for preparation of the sample are given in Chapter Three, Section 3.2.

7.2 See Method 7000, Paragraph 7.2, Direct Aspiration.

8.0 QUALITY CONTROL

8.1 See Section 8.0 of Method 7000.

9.0 METHOD PERFORMANCE

9.1 The performance characteristics for an aqueous sample free of interferences are:

Optimum concentration range: 0.3-5 mg/L with a wavelength of 232.0 nm.
Sensitivity: 0.15 mg/L.
Detection limit: 0.04 mg/L.

9.2 In a single laboratory, analysis of a mixed industrial-domestic waste effluent, digested with Method 3010, at concentrations of 0.2, 1.0, and 5.0 mg/L gave standard deviations of ±0.011, ±0.02, and ±0.04, respectively. Recoveries at these levels were 100%, 97%, and 93%, respectively.

9.3 The data shown in Table 1 were obtained from records of state and contractor laboratories. The data are intended to show the precision of the combined sample preparation and analysis method.

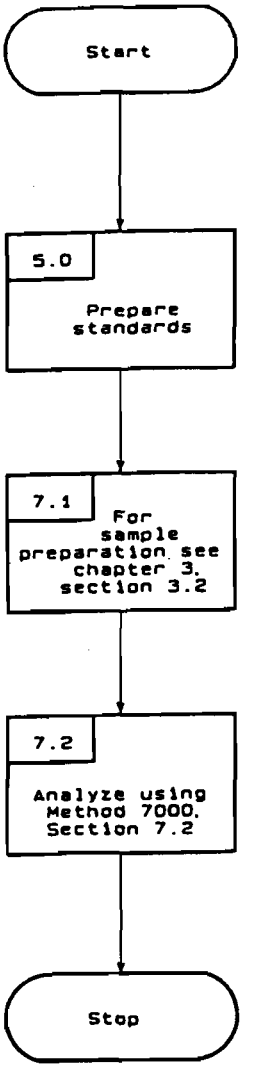
10.0 REFERENCES

1. Methods for Chemical Analysis of Water and Wastes, EPA-600/4-82-055, December 1982, Method 249.1

2. Gaskill, A., Compilation and Evaluation of RCRA Method Performance Data, Work Assignment No. 2, EPA Contract No. 68-01-7075, September 1986.

TABLE 1. METHOD PERFORMANCE DATA

Sample Matrix	Preparation Method	Laboratory Replicates
Wastewater treatment sludge	3050	13,000, 10,400 ug/g


Start
5.0
Prepare standards
7.1
For sample preparation see chapter 3, section 3.2
7.2
Analyze using Method 7000, Section 7.2
Stop

METHOD 7550

OSMIUM (ATOMIC ABSORPTION, DIRECT ASPIRATION)

1.0 SCOPE AND APPLICATION

1.1 Method 7550 is an atomic absorption procedure approved for determining the concentration of osmium in wastes, mobility procedure extracts, soils, and ground water. All samples must be subjected to an appropriate dissolution step prior to analysis.

2.0 SUMMARY OF METHOD

2.1 Prior to analysis by Method 7550, samples must be prepared for direct aspiration. The method of sample preparation will vary according to the sample matrix. Aqueous samples are subjected to the acid digestion procedure discussed in this method. Sludge samples are prepared using the procedure described in Method 3050. For samples containing oils, greases, or waxes, the procedure described in Method 3040 may be applicable. Due to the very volatile nature of some osmium compounds, the applicability of a method to a sample must be verified by means of spiked samples or standard reference materials, or both.

2.2 Following the appropriate dissolution of the sample, a representative aliquot is aspirated into a nitrous oxide/acetylene flame. The resulting absorption of hollow cathode radiation will be proportional to the osmium concentration. Background correction must be employed for all analyses.

2.3 The typical detection limit for this method is 0.3 mg/L; typical sensitivity is 1 mg/L.

3.0 INTERFERENCES

3.1 Background correction is required because nonspecific absorption and light scattering can be significant at the analytical wavelength.

3.2 Due to the volatility of osmium, standards must be made on a daily basis, and the applicability of sample-preparation techniques must be verified for the sample matrices of interest.

3.3 Samples and standards should be monitored for viscosity differences that may alter the aspiration rate.

3.4 Osmium and its compounds are extremely toxic; therefore, extreme care must be taken to ensure that samples and standards are handled properly and that all exhaust gases are properly vented.

4.0 APPARATUS AND MATERIALS

4.1 Atomic absorption spectrophotometer: Single- or dual-channel, single- or double-beam instrument with a grating monochromator, photomultiplier detector, adjustable slits, and provisions for background correction.

4.2 Osmium hollow cathode lamp.

4.3 Strip-chart recorder (optional).

5.0 REAGENTS

5.1 ASTM Type II water (ASTM D1193): Water should be monitored for impurities.

5.2 Concentrated nitric acid (HNO_3): Acid should be analyzed to determine levels of impurities. If a method blank using the acide is <MDL, the acid can be used.

5.3 Osmium standard stock solution (1,000 mg/L): Procure a certified aqueous standard from a supplier and verify by comparison with a second standard. If necessary, standards can be made from osmium compounds. However, due to the toxicity of these compounds, this approach is not advised.

5.4 Osmium working standards: Prepare dilution of the stock solution at the time of analysis. These standards should be prepared to contain 1% (v/v) HNO_3 and 1% (v/v) H_2SO_4.

5.5 Air: Cleaned and dried through a suitable filter to remove oil, water, and other foreign substances. The source may be a compressor or a cylinder of industrial-grade compressed air.

5.6 Acetylene: Should be of high purity. Acetone, which is usually present in acetylene cylinders, can be prevented from entering and affecting flame conditions by replacing the cylinder before the pressure has fallen to 50 psig.

5.7 Nitrous oxide: Cylinder suitable for instrumental analysis.

6.0 SAMPLE COLLECTION, PRESERVATION, AND HANDLING

6.1 All samples must have been collected using a sampling plan that addresses the considerations discussed in Chapter Nine of this manual.

6.2 All sample containers must be prewashed with detergents, acids, and Type II water. Plastic and glass containers are both suitable.

6.3 Aqueous samples must be acidified to a pH <2 with HNO_3.

6.4 Nonaqueous samples shall be refrigerated, when possible, and analyzed as soon as possible.

7.0 PROCEDURE

7.1 Sample preparation: Aqueous samples should be prepared according to the procedure described in Paragraph 7.2. Sludge-type samples should be prepared according to Method 3050; samples containing oils, greases, or waxes may be prepared according to Method 3040. The applicability of a sample preparation technique to a new matrix type must be demonstrated by analyzing spiked samples, relevant standard reference materials, or both.

7.2 Sample preparation of aqueous samples:

7.2.1 Transfer a representative 100-mL aliquot of the well-mixed sample to a Griffin beaker and add 1 mL of concentrated HNO_3.

7.2.2 Place the beaker on a steam bath or hot plate and warm for 15 min. Cool the beaker and, if necessary, filter or centrifuge to remove insoluble material.

7.2.3 Add 1 mL of concentrated H_2SO_4 and adjust the volume back to 100 mL. The sample is now ready for analysis.

7.3 The 290.0-nm wavelength line and background correction shall be employed.

7.4 A fuel-rich nitrous oxide/acetylene flame shall be used.

7.5 Follow the manufacturer's operating instructions for all other instrument parameters.

7.6 Either (1) run a series of osmium standards and construct a calibration curve by plotting the concentrations of the standards against the absorbances, or (2) for the method of standard additions, plot added concentration versus absorbance. For instruments that read directly in concentration, set the curve corrector to read out the proper concentration.

7.7 Analyze all EP extracts, all samples analyzed as part of a delisting petition, and all samples that suffer from matrix interferences by the method of standard additions.

7.8 Duplicates, spiked samples, and check standards should be routinely analyzed.

7.9 Calculate metal concentrations: (1) by the method of standard additions, (2) from a calibration curve, or (3) directly from the instrument's concentration read-out. All dilution or concentration factors must be taken into account.

8.0 QUALITY CONTROL

8.1 All quality control data should be maintained and available for easy reference or inspection.

8.2 Calibration curves must be composed of a minimum of a blank and three standards. A calibration curve should be made for every hour of continuous sample analysis.

8.3 Dilute samples if they are more concentrated than the highest standard or if they fall on the plateau of a calibration curve.

8.4 Employ a minimum of one blank per sample batch to determine if contamination or any memory effects are occurring.

8.5 Verify calibration with an independently prepared check standard every 15 samples.

8.6 Run one spike duplicate sample for every 10 samples. A duplicate sample is a sample brought through the entire sample preparation and analytical process.

8.7 The method of standard additions (see Method 7000, Section 8.7) shall be used for the analysis of all EP extracts, on all analyses submitted as part of a delisting petition, and whenever a new sample matrix is being analyzed.

9.0 METHOD PERFORMANCE

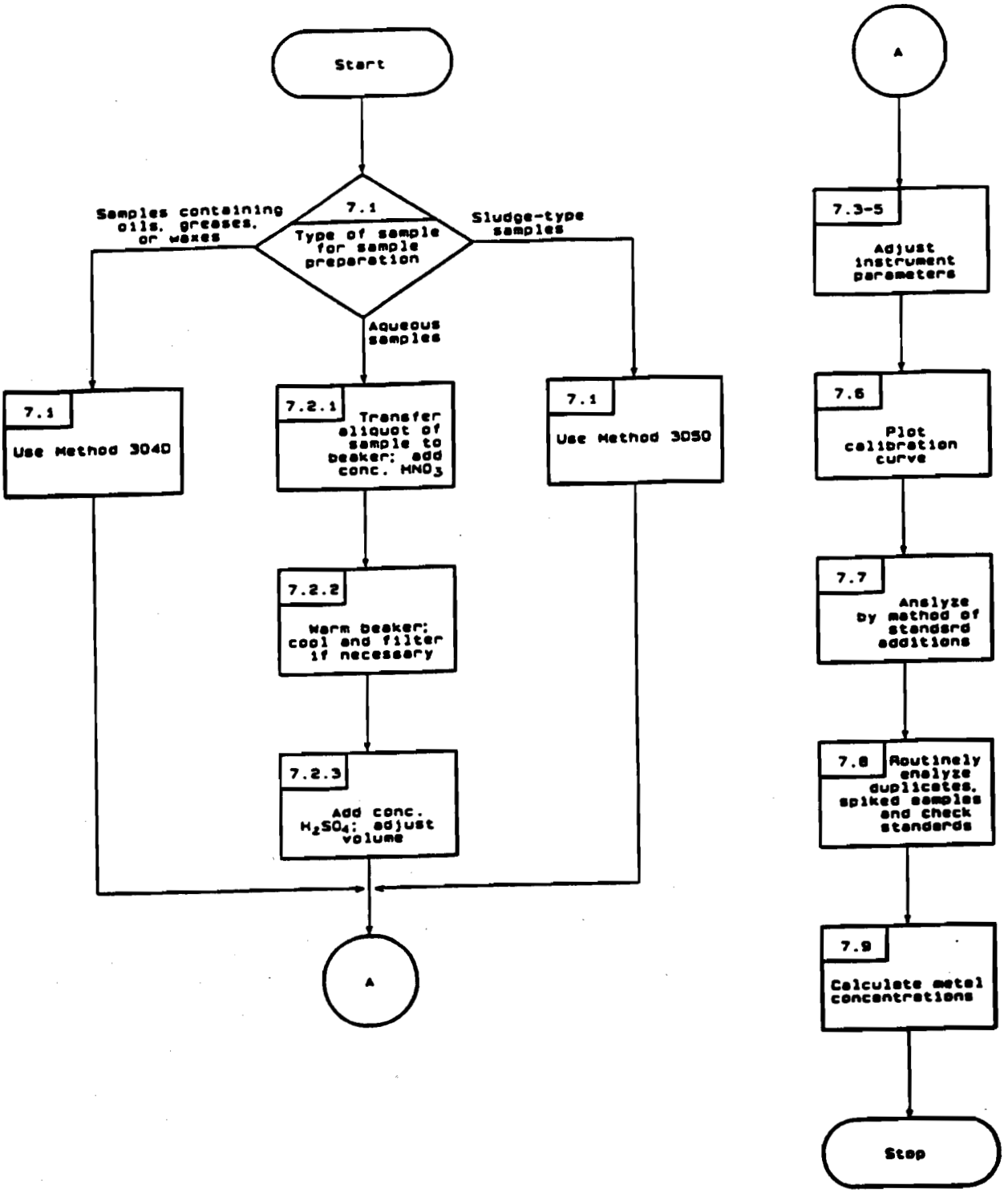
9.1 Precision and accuracy data are not available at this time.

10.0 REFERENCES

1. Methods for Chemical Analysis of Water and Wastes, EPA-600/4-82-055, December 1982, Method 252.1.

METHOD 7550

OSMIUM (ATOMIC ABSORPTION, DIRECT ASPIRATION METHOD)



Revision 0
Date September 1986

METHOD 7610

POTASSIUM (ATOMIC ABSORPTION, DIRECT ASPIRATION)

1.0 SCOPE AND APPLICATION

1.1 See Section 1.0 of Method 7000.

2.0 SUMMARY OF METHOD

2.1 See Section 2.0 of Method 7000.

3.0 INTERFERENCES

3.1 See Section 3.0 of Method 7000 if interferences are suspected.

3.2 In air/acetylene or other high-temperature flames (>2800°C), potassium can experience partial ionization, which indirectly affects absorption sensitivity. The presence of other alkali salts in the sample can reduce this ionization and thereby enhance analytical results. The ionization-suppressive effect of sodium is small if the ratio of Na to K is under 10. Any enhancement due to sodium can be stabilized by adding excess sodium (1,000 ug/mL) to both sample and standard solutions. If more stringent control of ionization is required, the addition of cesium should be considered. Reagent blanks should be analyzed to correct for potassium impurities in the buffer stock.

4.0 APPARATUS AND MATERIALS

4.1 For basic apparatus, see Section 4.0 of Method 7000.

4.2 Instrument parameters (general):

4.2.1 **Potassium hollow cathode lamp.**
4.2.2 **Wavelength:** 766.5 nm.
4.2.3 **Fuel:** Acetylene.
4.2.4 **Oxidant:** Air.
4.2.5 **Type of flame:** Slightly oxidizing (fuel lean).
4.2.6 **Background correction:** Not required.

5.0 REAGENTS

5.1 See Section 5.0 of Method 7000.

5.2 Preparation of standards:

5.2.1 **Stock solution:** Dissolve 1.907 g of potassium chloride, KCl (analytical reagent grade), dried at 110°C in Type II water and dilute to 1 liter with Type II water. Alternatively, procure a certified standard from a supplier and verify by comparison with a second standard.

5.2.2 Prepare dilutions of the stock solution to be used as calibration standards at the time of analysis. The calibration standards should be prepared using the same type of acid and at the same concentration as will result in the sample to be analyzed after processing.

6.0 SAMPLE COLLECTION, PRESERVATION, AND HANDLING

6.1 See Chapter Three, Section 3.1.3, Sample Handling and Preservation.

7.0 PROCEDURE

7.1 Sample preparation: The procedures for preparation of the sample are given in Chapter Three, Section 3.2.

7.2 See Method 7000, Paragraph 7.2, Direct Aspiration.

8.0 QUALITY CONTROL

8.1 See Section 8.0 of Method 7000.

9.0 METHOD PERFORMANCE

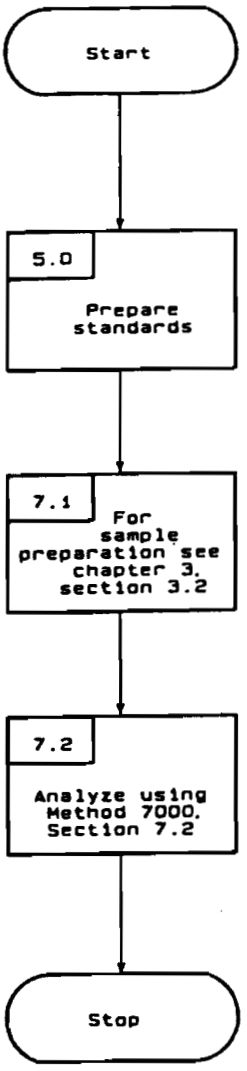
9.1 The performance characteristics for an aqueous sample free of interferences are:

Optimum concentration range: 0.1-2 mg/L with a wavelength of 766.5 nm.
Sensitivity: 0.04 mg/L.
Detection limit: 0.01 mg/L.

9.2 In a single laboratory, analysis of a mixed industrial-domestic waste effluent, digested with Method 3010, at concentrations of 1.6 and 6.3 mg/L gave standard deviations of $\pm$0.2 and $\pm$0.5, respectively. Recoveries at these levels were 103% and 102%, respectively.

10.0 REFERENCES

1. Methods for Chemical Analysis of Water and Wastes, EPA-600/4-82-055, December 1982, Method 258.1.


Start
5.0
Prepare standards
7.1
For sample preparation see chapter 3, section 3.2
7.2
Analyze using Method 7000, Section 7.2
Stop

METHOD 7740

SELENIUM (ATOMIC ABSORPTION, FURNACE TECHNIQUE)

1.0 SCOPE AND APPLICATION

1.1 Method 7740 is an atomic absorption procedure approved for determining the concentration of selenium in wastes, mobility-procedure extracts, soils, and ground water. All samples must be subjected to an appropriate dissolution step prior to analysis.

2.0 SUMMARY OF METHOD

2.1 Prior to analysis by Method 7740, samples must be prepared in order to convert organic forms of selenium to inorganic forms, to minimize organic interferences, and to convert samples to suitable solutions for analysis. The sample-preparation procedure varies, depending on the sample matrix. Aqueous samples are subjected to the acid-digestion procedure described in this method. Sludge samples are prepared using the procedure described in Method 3050.

2.2 Following the appropriate dissolution of the sample, a representative aliquot is placed manually or by means of an automatic sampler into a graphite tube furnace. The sample aliquot is then slowly evaporated to dryness, charred (ashed), and atomized. The absorption of lamp radiation during atomization will be proportional to the selenium concentration.

2.3 The typical detection limit for this method is 2 ug/L.

3.0 INTERFERENCES

3.1 Elemental selenium and many of its compounds are volatile; therefore, samples may be subject to losses of selenium during sample preparation. Spike samples and relevant standard reference materials should be processed to determine if the chosen dissolution method is appropriate.

3.2 Likewise, caution must be employed during the selection of temperature and times for the dry and char (ash) cycles. A nickel nitrate solution must be added to all digestates prior to analysis to minimize volatilization losses during drying and ashing.

3.3 In addition to the normal interferences experienced during graphite furnace analysis, selenium analysis can suffer from severe nonspecific absorption and light scattering caused by matrix components during atomization. Selenium analysis is particularly susceptible to these problems because of its low analytical wavelength (196.0 nm). Simultaneous background correction is required to avoid erroneously high results. High iron levels can give overcorrection with deuterium background. Zeeman background correction can be useful in this situation.

3.4 If the analyte is not completely volatilized and removed from the furnace during atomization, memory effects will occur. If this situation is detected, the tube should be cleaned by operating the furnace at full power at regular intervals in the analytical scheme.

3.5 Selenium analysis suffers interference from chlorides (>800 mg/L) and sulfate (>200 mg/L). The addition of nickel nitrate such that the final concentration is 1% nickel will lessen this interference.

4.0 APPARATUS AND MATERIALS

4.1 250-mL Griffin beaker.

4.2 10-mL volumetric flasks.

4.3 Atomic absorption spectrophotometer: Single- or dual-channel, single- or double-beam instrument with a grating monochromator, photomultiplier detector, adjustable slits, a wavelength range of 190-800 nm, and provisions for simultaneous background correction and interfacing with a strip-chart recorder.

4.4 Selenium hollow cathode lamp, or electrodeless discharge lamp (EDL): EDLs provide better sensitivity for the analysis of Se.

4.5 Graphite furnace: Any graphite furnace device with the appropriate temperature and timing controls.

4.6 Strip-chart recorder: A recorder is strongly recommended for furnace work so that there will be a permanent record and so that any problems with the analysis, such as drift, incomplete atomization, losses during charring, changes in sensitivity, etc., can easily be recognized.

4.7 Pipets: Microliter with disposable tips. Sizes can range from 5 to 1,000 uL, as required.

5.0 REAGENTS

5.1 ASTM Type II water (ASTM D1193): Water should be monitored for impurities.

5.2 Concentrated nitric acid (HNO_3): Acid should be analyzed to determine levels of impurities. If a method blank made with the acid is <MDL, the acid can be used.

5.3. Hydrogen peroxide (30%): Oxidant should be analyzed to determine levels of impurities. If a method blank made with the oxidant is <MDL, the oxidant can be used.

5.4 Selenium standard stock solution (1,000 mg/L): Either procure a certified aqueous standard from a supplier and verify by comparison with a second standard, or dissolve 0.3453 g of selenious acid (actual assay 94.6% H_2SeO_3, analytical reagent grade) or equivalent in Type II water and dilute to 200 mL.

5.5 Nickel nitrate solution (5%): Dissolve 24.780 g of ACS reagent grade $Ni(NO_3)_2 \cdot 6H_2O$ or equivalent in Type II water and dilute to 100 mL.

5.6 Nickel nitrate solution (1%): Dilute 20 mL of the 5% nickel nitrate to 100 mL with Type II water.

5.7 Selenium working standards: Prepare dilutions of the stock solution to be used as calibration standards at the time of the analysis. Withdraw appropriate aliquots of the stock solution, add 1 mL of concentrated HNO_3, 2 mL of 30% H_2O_2, and 2 mL of the 5% nickel nitrate solution. Dilute to 100 mL with Type II water.

5.8 Air: Cleaned and dried through a suitable filter to remove oil, water, and other foreign substances. The source may be a compressor or a cylinder of industrial-grade compressed air.

5.9 Hydrogen: Suitable for instrumental analysis.

6.0 SAMPLE COLLECTION, PRESERVATION, AND HANDLING

6.1 All samples must have been collected using a sampling plan that addresses the considerations discussed in Chapter Nine of this manual.

6.2 All sample containers must be prewashed with detergents, acids, and Type II water. Plastic and glass containers are both suitable.

6.3 Special containers (e.g., containers used for volatile organic analysis) may have to be used if very volatile selenium compounds are to be analyzed.

6.4 Aqueous samples must be acidified to a pH of <2 with nitric acid.

6.5 Nonaqueous samples shall be refrigerated, when possible, and analyzed as soon as possible.

7.0 PROCEDURE

7.1 Sample preparation: Aqueous samples should be prepared in the manner described in Steps 7.1.1 to 7.1.3. Sludge-type samples should be prepared according to Method 3050. The applicability of a sample-preparation technique to a new matrix type must be demonstrated by analyzing spiked samples and/or relevant standard reference materials.

7.1.1 Transfer 100 mL of well-mixed sample to a 250-mL Griffin beaker; add 2 mL of 30% H_2O_2 and sufficient concentrated HNO_3 to result in an acid concentration of 1% (v/v). Heat for 1 hr at 95°C or until the volume is slightly less than 50 mL.

7.1.2 Cool and bring back to 50 mL with Type II water.

7.1.3 Pipet 5 mL of this digested solution into a 10-mL volumetric flask, add 1 mL of the 1% nickel nitrate solution, and dilute to 10 mL with Type II water. The sample is now ready for injection into the furnace.

7.2 The 196.0-nm wavelength line and a background correction system must be employed. Follow the manufacturer's suggestions for all other spectrophotometer parameters.

7.3 Furnace parameters suggested by the manufacturer should be employed as guidelines. Because temperature-sensing mechanisms and temperature controllers can vary between instruments or with time, the validity of the furnace parameters must be periodically confirmed by systematically altering the furnace parameters while analyzing a standard. In this manner, losses of analyte due to overly high temperature settings or losses in sensitivity due to less than optimum settings can be minimized. Similar verification of furnace parameters may be required for complex sample matrices.

7.4 Inject a measured uL-aliquot of sample into the furnace and atomize. If the concentration found is greater than the highest standard, the sample should be diluted in the same acid matrix and reanalyzed. The use of multiple injections can improve accuracy and help detect furnace pipetting errors.

7.5 Analyze all EP extracts, all samples analyzed as part of a delisting petition, and all samples that suffer from matrix interferences by the method of standard additions.

7.6 Run a check standard after approximately every 10 sample injections. Standards are run in part to monitor the life and performance of the graphite tube. Lack of reproducibility or significant change in the signal for the standard indicates that the tube should be replaced.

7.7 Duplicates, spiked samples, and check standards should be analyzed every 20 samples.

7.8 Calculate metal concentrations: (1) by the method of standard additions, (2) from a calibration curve, or (3) directly from the instrument's concentration read-out. All dilution or concentration factors must be taken into account.

8.0 QUALITY CONTROL

8.1 All quality control data should be maintained and available for easy reference or inspection.

8.2 Calibration curves must be composed of a minimum of a blank and three standards. A calibration curve should be made for every hour of continuous sample analysis.

8.3 Dilute samples if they are more concentrated than the highest standard or if they fall on the plateau of a calibration curve.

8.4 Employ a minimum of one blank per sample batch to determine if contamination or any memory effects are occurring.

8.5 Verify calibration with an independently prepared check standard every 15 samples.

8.6 Run one spike duplicate sample for every 10 samples. A duplicate sample is a sample brought through the entire sample preparation and analytical process.

8.7 The method of standard additions (see Method 7000, Section 8.7) shall be used for the analysis of all EP extracts, on all analyses submitted as part of a delisting petition, and whenever a new sample matrix is being analyzed.

9.0 METHOD PERFORMANCE

9.1 Precision and accuracy data are available in Method 270.2 of Methods for Chemical Analysis of Water and Wastes.

9.2 The data shown in Table 1 were obtained from records of state and contractor laboratories. The data are intended to show the precision of the combined sample preparation and analysis method.

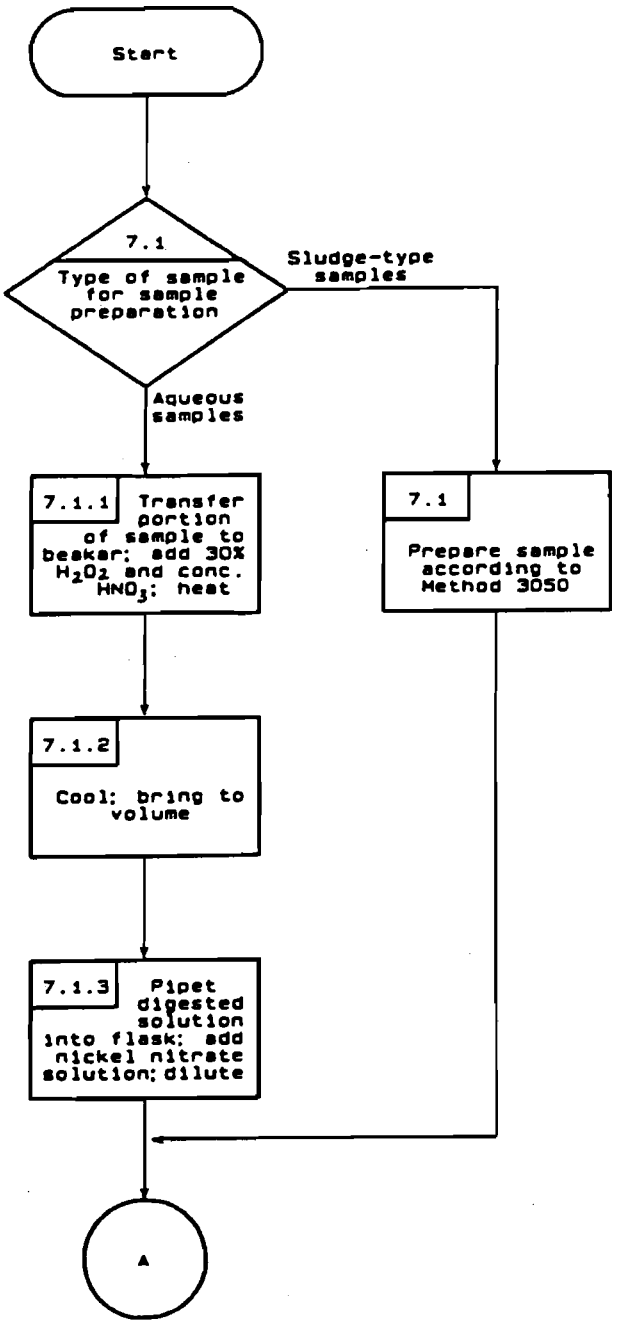
10.0 REFERENCES

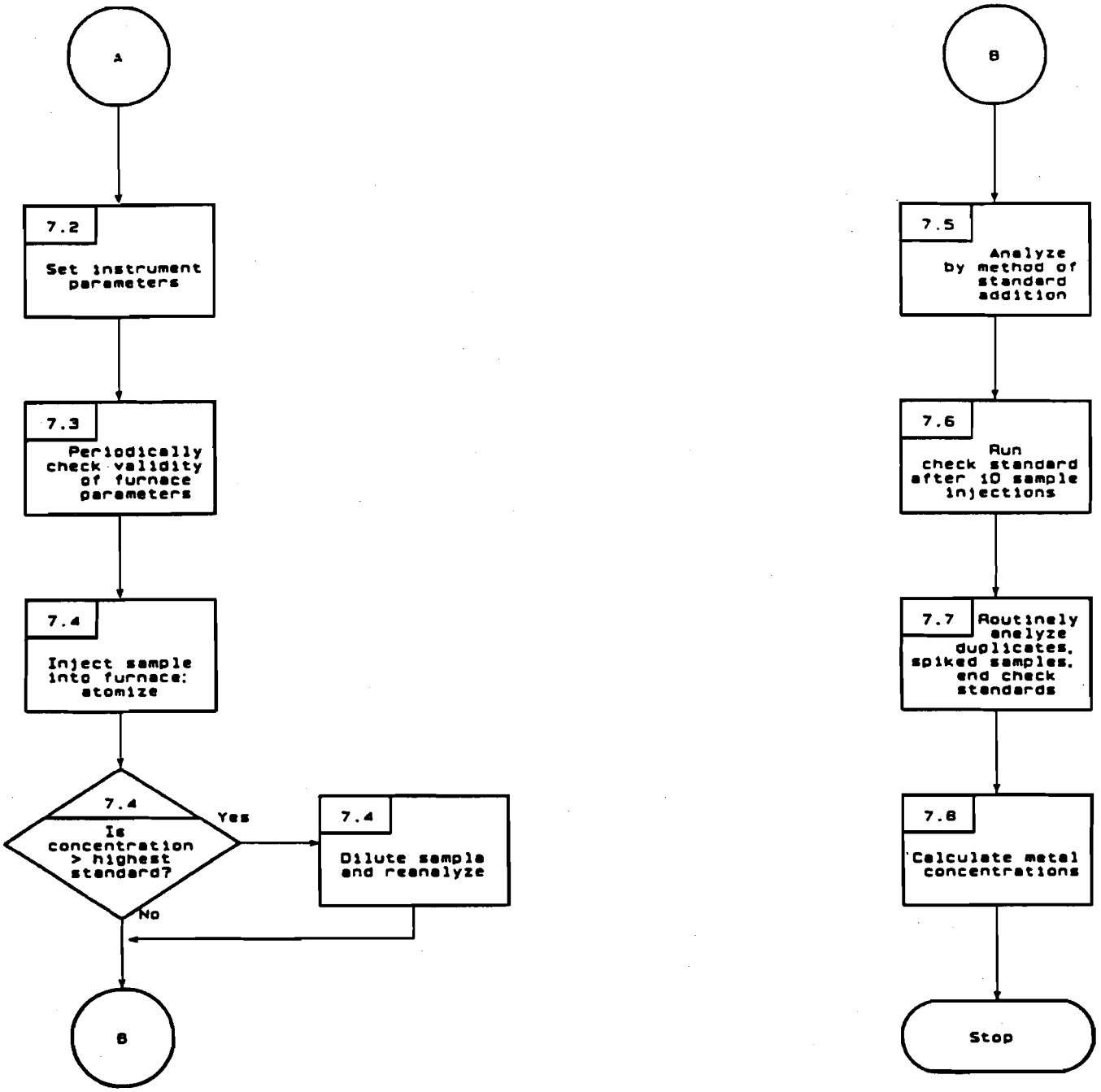
1. Methods for Chemical Analysis of Water and Wastes, EPA-600/4-82-055, December 1982, Method 270.2.

2. Gaskill, A., Compilation and Evaluation of RCRA Method Performance Data, Work Assignment No. 2, EPA Contract No. 68-01-7075, September 1986.

TABLE 1. METHOD PERFORMANCE DATA

Sample Matrix	Preparation Method	Laboratory Replicates
Emission control dust	3050	14, 11 ug/g


Start
7.1
Type of sample for sample preparation
Sludge-type samples
Aqueous samples
7.1.1 Transfer portion of sample to beaker; add 30% H_2O_2 and conc. HNO_3; heat
7.1
Prepare sample according to Method 3050
7.1.2
Cool; bring to volume
7.1.3 Pipet digested solution into flask; add nickel nitrate solution; dilute
A


A
7.2
Set instrument parameters
7.3
Periodically check validity of furnace parameters
7.4
Inject sample into furnace: atomize
7.4
Is concentration > highest standard?
Yes
No
7.4
Dilute sample and reanalyze
B
B
7.5
Analyze by method of standard addition
7.6
Run check standard after 10 sample injections
7.7
Routinely analyze duplicates, spiked samples, and check standards
7.8
Calculate metal concentrations
Stop

METHOD 7741A

SELENIUM (ATOMIC ABSORPTION, GASEOUS HYDRIDE)

1.0 SCOPE AND APPLICATION

1.1 Method 7741 is an atomic absorption procedure that is approved for determining the concentration of selenium in wastes, mobility-procedure extracts, soils, and ground water, provided that the sample matrix does not contain high concentrations of chromium, copper, mercury, silver, cobalt, or molybdenum. All samples must be subjected to an appropriate dissolution step prior to analysis. Spiked samples and relevant standard reference materials are employed to determine applicability of the method to a given waste. If interferences are present the analyst should consider using Method 7740.

2.0 SUMMARY OF METHOD

2.1 Samples are prepared according to the nitric/sulfuric acid digestion procedure described in this method. Next, the selenium in the digestate is reduced to Se(IV) with tin chloride. The Se(IV) is then converted to a volatile hydride with hydrogen produced from a zinc/HCl or sodium borohydrate/HCl reaction.

2.2 The volatile hydride is swept into an argon-hydrogen flame located in the optical path of an atomic absorption spectrophotometer; the resulting absorbance is proportional to the selenium concentration.

2.3 The typical detection limit for this method is 0.002 mg/L.

3.0 INTERFERENCES

3.1 High concentrations of chromium, cobalt, copper, mercury, molybdenum, nickel, and silver can cause analytical interferences.

3.2 Traces of nitric acid left following the sample work-up can result in analytical interferences. Nitric acid must be distilled off the sample by heating the sample until fumes of SO_3 are observed.

3.3 Elemental selenium and many of its compounds are volatile; therefore, certain samples may be subject to losses of selenium during sample preparation.

4.0 APPARATUS AND MATERIALS

4.1 100-mL beaker.

4.2 Electric hot plate or equivalent - Adjustable and capable of maintaining a temperature of 90-95°C.

4.3 A commercially available zinc slurry hydride generator or a generator constructed from the following material (see Figure 1):

4.3.1 Medicine dropper: Fitted into a size "0" rubber stopper capable of delivering 1.5 mL.

4.3.2 Reaction flask: 50-mL, pear-shaped, with two 14/20 necks (Scientific Glass, JM-5835).

4.3.3 Gas inlet-outlet tube: Constructed from a micro cold-finger condenser (JM-3325) by cutting the portion below the 14/20 ground-glass joint.

4.3.4 Magnetic stirrer: To homogenize the zinc slurry.

4.3.5 Polyethylene drying tube: 10-cm, filled with glass wool to prevent particulate matter from entering the burner.

4.3.6 Flow meter: Capable of measuring 1 liter/min.

4.4 Atomic absorption spectrophotometer: Single or dual channel, single- or double-beam instrument with a grating monochromator, photomultiplier detector, adjustable slits, a wavelength range of 190-800 nm, and provisions for interfacing with a strip-chart recorder and simultaneous background correction.

4.5 Burner: Recommended by the particular instrument manufacturer for the argon-hydrogen flame.

4.6 Selenium hollow cathode lamp or electrodeless discharge lamp.

4.7 Strip-chart recorder (optional).

5.0 REAGENTS

5.1 Reagent water: Water should be monitored for impurities. Reagent water will be interference free. All references to water will refer to reagent water.

5.2 Concentrated nitric acid: Acid should be analyzed to determine levels of impurities. If a method blank made with the acid is <MDL, the acid can be used.

5.3 Concentrated sulfuric acid: Acid should be analyzed to determine levels of impurities. If a method blank made with the acid is <MDL, the acid can be used.

5.4 Concentrated hydrochloric acid: Acid should be analyzed to determine levels of impurities. If a method blank made with the acid is <MDL, the acid can be used.

5.5 Diluent: Add 100 mL 18 N H_2SO_4 and 400 mL concentrated HCl to 400 mL reagent water and dilute to a final volume of 1 liter with reagent water.

5.6 Potassium iodide solution: Dissolve 20 g KI in 100 mL reagent water.

5.7 Stannous chloride solution: Dissolve 100 g $SnCl_2$ in 100 mL of concentrated HCl.

5.8 Selenium standard stock solution: 1,000 mg/L solution may be purchased, or prepared as follows: Dissolve 0.3453 g of selenious acid (assay 94.6% of H_2SeO_3) in reagent water. Add to a 200-mL volumetric flask and bring to volume (1 mL = 1 mg Se).

6.0 SAMPLE COLLECTION, PRESERVATION, AND HANDLING

6.1 All samples must have been collected using a sampling plan that addresses the considerations discussed in Chapter Nine of this manual.

6.2 All sample containers must be prewashed with detergents, acids, and reagent water. Plastic and glass containers are both suitable.

6.3 Special containers (e.g., containers used for volatile organic analysis) may have to be used if very volatile selenium compounds are to be analyzed.

6.4 Aqueous samples must be acidified to a pH of <2 with nitric acid.

6.5 Nonaqueous samples shall be refrigerated, when possible, and analyzed as soon as possible.

7.0 PROCEDURE

7.1 Sample preparation:

7.1.1 To a 50-mL aliquot of digested sample (or, in the case of extracts, a 50-mL sample) add 10 mL of concentrated HNO_3 and 12 mL of 18 N H_2SO_4. Evaporate the sample on a hot plate until white SO_3 fumes are observed (a volume of about 20 mL). Do not let it char. If it chars, stop the digestion, cool, and add additional HNO_3. Maintain an excess of HNO_3 (evidence of brown fumes) and do not let the solution darken because selenium may be reduced and lost. When the sample remains colorless or straw yellow during evolution of SO_3 fumes, the digestion is complete.

> Caution: Venting reaction vessels should be done with caution and only under a fume hood or well ventilated area.

7.1.2 Cool the sample, add about 25 mL reagent water, and again evaporate to SO_3 fumes just to expel oxides of nitrogen. Cool. Add 40 mL concentrated HCl and bring to a volume of 100 mL with reagent water.

7.2 Prepare working standards from the standard stock solutions. The following procedures provide standards in the optimum range.

7.2.1 To prepare a working stock solution, pipet 1 mL standard stock solution (see Paragraph 5.8) into a 1-liter volumetric flask. Bring to volume with reagent water containing 1.5 mL concentrated HNO_3/liter. The concentration of this solution is 1 mg Se/L (1 mL = 1 ug Se).

7.2.2 Prepare six working standards by transferring 0, 0.5, 1.0, 1.5, 2.0, and 2.5 mL of the working stock solution (see Paragraph 7.2.1) into 100-mL volumetric flasks. Bring to volume with diluent. The concentrations of these working standards are 0, 5, 10, 15, 20, and 25 ug Se/L.

7.3 Standard additions:

7.3.1 Take the 15-, 20-, and 25-ug standards and transfer quantitatively 25 mL from each into separate 50-mL volumetric flasks. Add 10 mL of the prepared sample to each. Bring to volume with reagent water containing 1.5 mL HNO_3/liter.

7.3.2 Add 10 mL of prepared sample to a 50-mL volumetric flask. Bring to volume with reagent water containing 1.5 mL HNO_3/liter. This is the blank.

7.4 Follow the manufacturer's instructions for operating an argon-hydrogen flame. The argon-hydrogen flame is colorless; therefore, it may be useful to aspirate a low concentration of sodium to ensure that ignition has occurred.

7.5 The 196.0-nm wavelength shall be used for the analysis of selenium.

7.6 Transfer a 25-mL portion of the digested sample or standard to the reaction vessel. Add 0.5 mL $SnCl_2$ solution. Allow at least 10 min for the metal to be reduced to its lowest oxidation state. Attach the reaction vessel to the special gas inlet-outlet glassware. Fill the medicine dropper with 1.50 mL sodium borohydrate or zinc slurry that has been kept in suspension with the magnetic stirrer. Firmly insert the stopper containing the medicine dropper into the side neck of the reaction vessel. Squeeze the bulb to introduce the zinc slurry or sodium borohydrate into the sample or standard solution. The metal hydride will produce a peak almost immediately. When the recorder pen returns partway to the base line, remove the reaction vessel.

8.0 QUALITY CONTROL

8.1 Refer to section 8.0 of Method 7000.

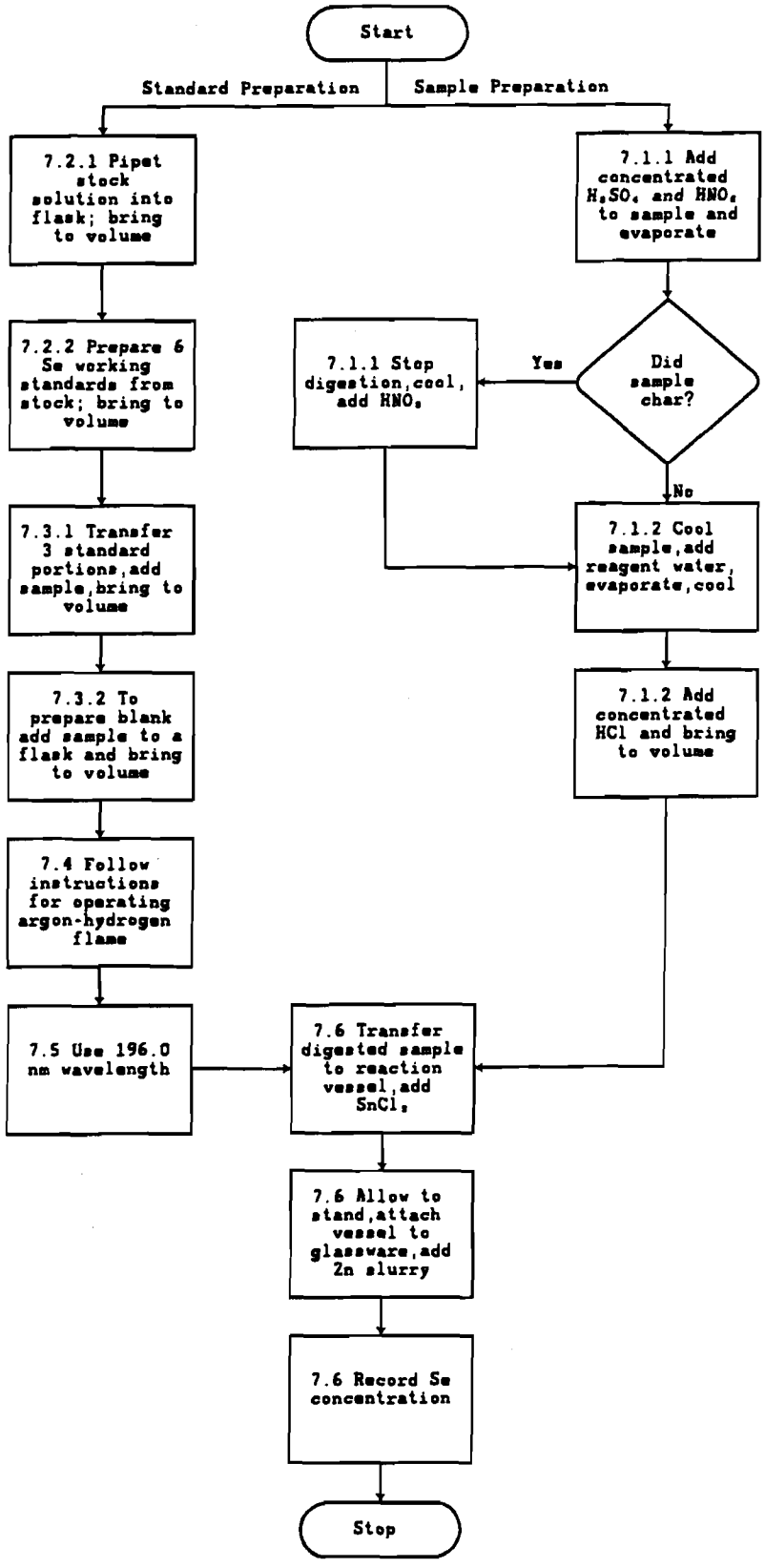
9.0 METHOD PERFORMANCE

9.1 Precision and accuracy data are available in Method 270.3 of Methods for Chemical Analysis of Water and Wastes.

10.0 REFERENCES

1. Methods for Chemical Analysis of Water and Wastes, EPA-600/4-82-055, December 1982, Method 270.3.

METHOD 7741A
SELENIUM (ATOMIC ABSORPTION, GASEOUS HYDRIDE)



METHOD 7742

SELENIUM (ATOMIC ABSORPTION, BOROHYDRIDE REDUCTION)

1.0 SCOPE AND APPLICATION

1.1 Method 7742 is an atomic absorption procedure for determining 3 µg/L to 750 µg/L concentrations of selenium in wastes, mobility procedure extracts, soils, and ground water. Method 7742 is approved for sample matrices that contain a total of up to 1000 mg/L concentrations of cobalt, copper, iron, mercury, and nickel. A solid sample can contain up to 10% by weight of the interferents before exceeding 1000 mg/L in a digested sample. All samples including aqueous matrices must be subjected to an appropriate dissolution step prior to analysis. Spiked samples and relevant standard reference materials are employed to determine the applicability of the method to a given waste.

2.0 SUMMARY OF METHOD

2.1 Samples are prepared according to the nitric acid digestion procedure described in Method 3010 for aqueous and extract samples and the nitric/peroxide/hydrochloric acid digestion procedure described in Method 3050 (furnace AA option) for sediments, soils, and sludges. Excess peroxide is removed by evaporating samples to near-dryness at the end of the digestion followed by dilution to volume and degassing the samples upon addition of urea. The selenium is converted to the +4 oxidation state during digestion in HCl. After a 1:10 dilution, selenium is then converted to its volatile hydride using hydrogen produced from the reaction of the acidified sample with sodium borohydride in a continuous-flow hydride generator.

2.2 The volatile hydrides are swept into, and decompose in, a heated quartz absorption cell located in the optical path of an atomic absorption spectrophotometer. The resulting absorption of the lamp radiation is proportional to the selenium concentration.

2.3 The typical detection limit for this method is 3 µg/L.

3.0 INTERFERENCES

3.1 Very high (>1000 mg/L) concentrations of cobalt, copper, iron, mercury, and, nickel can cause analytical interferences through precipitation as reduced metals and associated blockage of transfer lines and fittings.

3.2 Traces of peroxides left following the sample work-up can result in analytical interferences. Peroxides must be removed by evaporating each sample to near-dryness followed by reacting each sample with urea and allowing sufficient time for degassing before analysis (see Sections 7.1 and 7.2).

3.3 Even after acid digestion, flame gases and organic compounds may remain in the sample. Flame gases and organic compounds can absorb at the analytical wavelengths and background correction should be used.

4.0 APPARATUS AND MATERIALS

4.1 Electric hot plate: Large enough to hold at least several 100 mL Pyrex digestion beakers.

4.2 A continuous-flow hydride generator: A commercially available continuous-flow sodium borohydride/HCl hydride generator or a generator constructed similarly to that shown in Figure 1 (P. S. Analytical or equivalent).

4.2.1 Peristaltic Pump: A four-channel, variable-speed peristaltic pump to permit regulation of liquid-stream flow rates (Ismatec Reglo-100 or equivalent). Pump speed and tubing diameters should be adjusted to provide the following flow rates: sample/blank flow = 4.2 mL/min; borohydride flow = 2.1 mL/min.

4.2.2 Sampling Valve (optional): A sampling valve (found in the P. S. Analytical Hydride Generation System or equivalent) that allows switching between samples and blanks (rinse solution) without introduction of air into the system will provide more signal stability.

4.2.3 Transfer Tubing and Connectors: Transfer tubing (1 mm I.D.), mixing T's, and connectors are made of fluorocarbon (PFA or TFM) and are of compatible sizes to form tight, leak-proof connections (Latchat, Technicon, etc. flow injection apparatus accessories or equivalent).

4.2.4 Mixing Coil: A 20-turn coil made by wrapping transfer tubing around a 1-cm diameter by 5-cm long plastic or glass rod (see Figure 1).

4.2.5 Mixing Coil Heater, if appropriate: A 250-mL Erlenmeyer flask containing 100 mL of water heated to boiling on a dedicated one-beaker hotplate (Corning PC-35 or equivalent). The mixing coil in 4.2.4 is immersed in the boiling water to speed kinetics of the hydride forming reactions and increase solubility of interfering reduced metal precipitates.

4.2.6 Gas-Liquid Separator: A glass apparatus for collecting and separating liquid and gaseous products (P. S. Analytical accessory or equivalent) which allows the liquid fraction to drain to waste and gaseous products above the liquid to be swept by a regulated carrier gas (argon) out of the cell for analysis. To avoid undue carrier gas dilution, the gas volume above the liquid should not exceed 20 mL. See Figure 1 for an acceptable separator shape.

4.2.7 Condensor: Moisture picked up by the carrier gas must be removed before encountering the hot absorbance cell. The moist carrier gas with the hydrides is dried by passing the gasses through a small (< 25 mL) volume condensor coil (Ace Glass Model 6020-02 or equivalent) that is cooled to 5°C by a water chiller (Neslab RTE-110 or equivalent). Cool tap-water in place of a chiller is acceptable.

4.2.8 Flow Meter/Regulator: A meter capable of regulating up to 1 L/min of argon carrier gas is recommended.

4.3 Absorbance Cell: A 17-cm or longer quartz tube T-cell (windowless is strongly suggested) is recommended, as shown in Figure 1 (Varian Model VGA-76 accessory or equivalent). The cell is held in place by a holder that positions the cell about 1 cm over a conventional AA air-acetylene burner head. In operation, the cell is heated to around 900°C.

4.4 Atomic absorption spectrophotometer: Single- or dual- channel, single- or double-beam instrument having a grating monochromator, photomultiplier detector, adjustable slits, a wavelength range of 190 to 800 nm, and provisions for interfacing with an appropriate recording device.

4.5 Burner: As recommended by the particular instrument manufacturer for an air-acetylene flame. An appropriate mounting bracket attached to the burner that suspends the quartz absorbance cell between 1 and 2 cm above the burner slot is required.

4.6 Selenium hollow cathode lamp or selenium electrodeless discharge lamp and power supply. Super-charged hollow-cathode lamps or EDL lamps are recommended for maximum sensitivity.

4.7 Strip-chart recorder (optional): Connect to output of spectrophotometer.

5.0 REAGENTS

5.1 Reagent water : Water must be monitored for impurities. Refer to Chapter 1 for definition of Reagent water.

5.2 Concentrated nitric acid (HNO_3): Acid must be analyzed to determine levels of impurities. If a method blank is <MDL, the acid can be used.

5.3 30% Hydrogen peroxide (H_2O_2): Peroxide must be a tin-free grade.

5.4 Concentrated hydrochloric acid (HCl): Acid must be analyzed to determine levels of impurities. If a method blank is <MDL, the acid can be used.

5.5 Diluent solution: A 3% HCl solution in reagent water must be prepared as a diluent solution if excessive levels of analytes or interfering metals are found in the undiluted samples.

5.6 Urea (H_2NCONH_2): A 5.00-g portion of reagent grade urea must be added to a 25-mL aliquot of each sample for removal of excess peroxide through degassing (see Section 7.2).

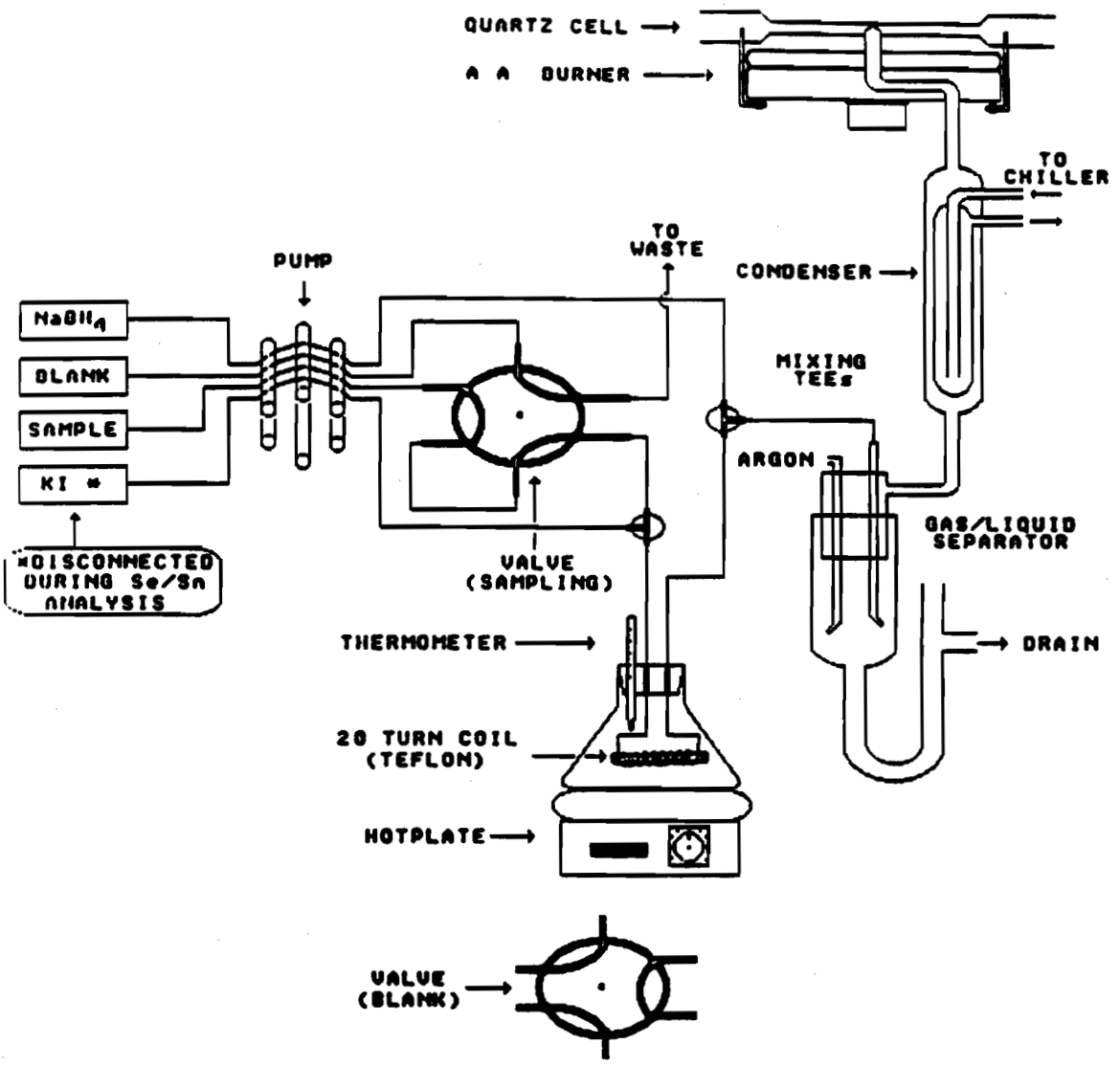


Figure 1. Continuous-flow sodium borohydride/hydride generator apparatus setup and an AAS sample introduction system

5.7 4% Sodium Borohydride ($NaBH_4$): A 4 % sodium borohydride solution (20 g reagent-grade $NaBH_4$ plus 2 g sodium hydroxide dissolved in 500 mL of reagent water) must be prepared for conversion of the selenium to its hydride.

5.8 Selenium solutions:

5.8.1 **Selenium standard stock solution** (1,000 mg/L): Either procure certified aqueous standards from a supplier and verify by comparison with a second standard, or dissolve 0.3453 g of selenious acid (assay 96.6% of H_2SeO_3) in 200 mL of reagent water (1 mL = 1 mg Se).

5.8.2 **Selenium working stock solution:** Pipet 1 mL selenium standard stock solution into a 1 L volumetric flask and bring to volume with reagent water containing 1.5 mL concentrated HNO_3/liter. The concentration of this solution is 1 mg Se/L (1 mL = 1 μg Se).

6.0 SAMPLE COLLECTION, PRESERVATION, AND HANDLING

6.1 All samples must have been collected using a sampling plan that addresses the considerations discussed in Chapter Nine of this manual.

6.2 All sample containers must be prewashed with detergents, acids, and reagent water. Plastic and glass containers are both suitable.

6.3 Special containers (e.g., containers used for volatile organic analysis) may have to be used if very volatile selenium compounds are suspected to be present in the samples.

6.4 Aqueous samples must be acidified to a pH of <2 with nitric acid.

6.5 Nonaqueous samples shall be refrigerated, when possible, and analyzed as soon as possible.

7.0 PROCEDURE

7.1 Place a 100-mL portion of an aqueous sample or extract or 1.000 g of a dried solid sample in a 250-mL digestion beaker. Digest aqueous samples and extracts according to Method 3010. Digest solid samples according to Method 3050 (furnace AA option) with the following modifications: add 5 mL of concentrated hydrochloric acid just prior to the final volume reduction stage to aid in conversion of selenium to its plus four state; the final volume reduction should be to less than 5 mL but not to dryness to adequately remove excess hydrogen peroxide (see note). After dilution to volume, further dilution with diluent may be necessary if the analyte is known to exceed 750 μg/L or if interferents are expected to exceed a total of 1000 mg/L in the digestate.

Note: For solid digestions, the volume reduction stage is critical to obtain accurate data. Close monitoring of each sample is necessary when this critical stage in the digestion is reached.

7.2 Prepare samples for hydride analysis by adding 1.00 g urea, and 20 mL concentrated HCl to a 5.00 mL aliquot of digested sample in a 50-mL volumetric flask. Heat in a water bath to dissolve salts and reduce selenium (at least 30 minutes is suggested). Bring flask to volume with reagent water before analyzing. A ten-fold dilution correction must be made in the final concentration calculations.

7.3 Prepare working standards from the standard stock selenium solution. Transfer 0, 0.5, 1.0, 1.5, 2.0, and 2.5 mL of standard to 100-mL volumetric flasks and bring to volume with diluent. These concentrations will be 0, 5, 10, 15, 20, and 25 μg Se/L.

7.4 If EP extracts (Method 1310) are being analyzed for selenium, the method of standard additions must be used. Spike appropriate amounts of working standard selenium solution to three 25 mL aliquots of each unknown. Spiking volumes should be kept less than 0.250 mL to avoid excessive spiking dilution errors.

7.5 Set up instrumentation and hydride generation apparatus and fill reagent containers. The sample and blank flows should be set around 4.2 mL/min and the borohydride flow around 2.1 mL/min. The argon carrier gas flow is adjusted to about 200 mL/min. For the AA, use the 196.0-nm wavelength and 2.0-nm slit width (or manufacturer's recommended slit-width) with background correction. Begin all flows and allow the instrument to warm-up according to the instrument manufacturer's instructions.

7.6 Place sample feed line into a prepared sample solution and start pump to begin hydride generation. Wait for a maximum steady-state signal on the strip-chart recorder. Switch to blank sample and watch for signal to decline to baseline before switching to the next sample and beginning the next analysis. Run standards first (low to high), then unknowns. Include appropriate QA/QC solutions, as required. Prepare calibration curves and convert absorbances to concentration. See following analytical flowchart.

CAUTION: The hydride of selenium is very toxic. Precautions must be taken to avoid inhaling the gas.

7.7 If the method of standard additions was employed, plot the measured concentration of the spiked samples and unspiked sample versus the spiked concentrations. The spiked concentration axis intercept will be the method of standard additions concentration. If the plot does not result in a straight line, a nonlinear interference is present. This problem can sometimes be overcome by dilution or addition of other reagents if there is some knowledge about the waste. If the method of standard additions was not required, then the concentration is determined from a standard calibration curve.

8.0 QUALITY CONTROL

8.1 Refer to Section 8.0 of Method 7000.

9.0 METHOD PERFORMANCE

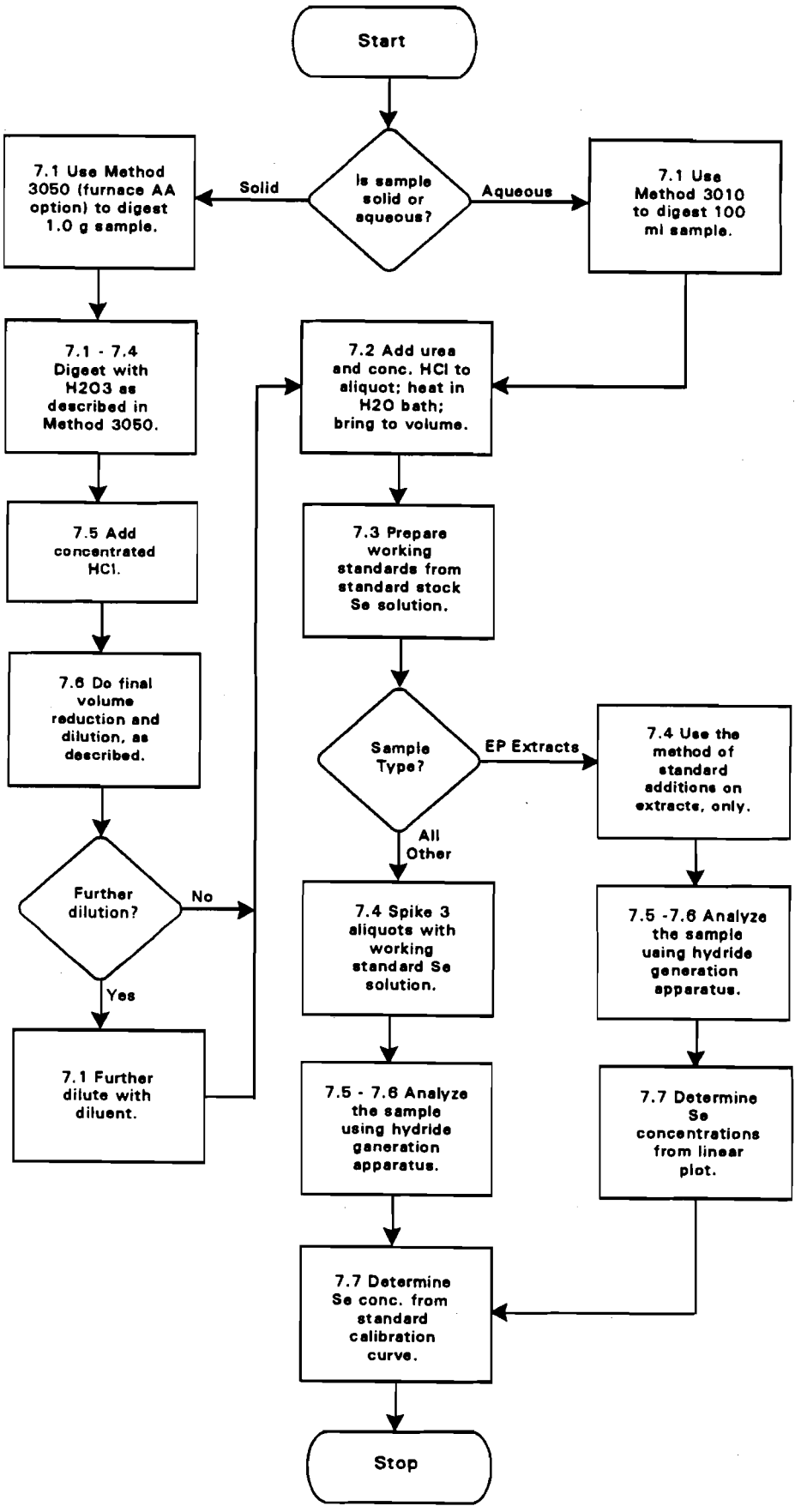
9.1 The relative standard deviation obtained by a single laboratory for 7 replicates of a contaminated soil was 18% for selenium at 8.2 ug/L in solution. The average percent recovery of the analysis of an 2 μg/L spike on ten different samples is 100.5% for selenium.

10.0 REFERENCES

1. Methods for Chemical Analysis of Water and Wastes, EPA-600/4-82-055, December 1982, Method 206.3.

2. "Evaluation of Hydride Atomic Absorption Methods for Antimony, Arsenic, Selenium, and Tin", an EMSL-LV internal report under Contract 68-03-3249, Job Order 70.16, prepared for T. A. Hinners by D. E. Dobb, and J. D. Lindner of Lockheed Engineering and Sciences Co., and L. V. Beach of the Varian Corporation.

METHOD 7742
SELENIUM (ATOMIC ABSORPTION, BOROHYDRIDE REDUCTION)



METHOD 7760A

SILVER (ATOMIC ABSORPTION, DIRECT ASPIRATION)

1.0 SCOPE AND APPLICATION

1.1 Method 7760 is an atomic absorption procedure approved for determining the concentration of silver (CAS Registry Number 7440-22-4) in wastes, mobility procedure extracts, soils, and ground water. All samples must be subjected to an appropriate dissolution step prior to analysis.

2.0 SUMMARY OF METHOD

2.1 Prior to analysis by Method 7760, samples must be prepared for direct aspiration. The method of sample preparation will vary according to the sample matrix. Aqueous samples are subjected to the acid-digestion procedure described in this method.

2.2 Following the appropriate dissolution of the sample, a representative aliquot is aspirated into an air/acetylene flame. The resulting absorption of hollow cathode radiation will be proportional to the silver concentration. Background correction must be employed for all analyses.

2.3 The typical detection limit for this method is 0.01 mg/L; typical sensitivity is 0.06 mg/L.

3.0 INTERFERENCES

3.1 Background correction is required because nonspecific absorption and light scattering may occur at the analytical wavelength.

3.2 Silver nitrate solutions are light-sensitive and have the tendency to plate out on container walls. Thus silver standards should be stored in brown bottles.

3.3 Silver chloride is insoluble; therefore, hydrochloric acid should be avoided unless the silver is already in solution as a chloride complex.

3.4 Samples and standards should be monitored for viscosity differences that may alter the aspiration rate.

4.0 APPARATUS AND MATERIALS

4.1 Atomic absorption spectrophotometer: Single- or dual-channel, single- or double-beam instrument with a grating monochromator, photomultiplier detector, adjustable slits, and provisions for background correction.

4.2 Silver hollow cathode lamp.

4.3 Strip-chart recorder (optional).

4.4 Graduated cylinder or equivalent.

4.5 Hot plate or equivalent - adjustable and capable of maintaining a temperature of 90-95°C.

4.6 Ribbed watchglasses or equivalent.

5.0 REAGENTS

5.1 Reagent grade chemicals shall be used in all tests. Unless otherwise indicated, it is intended that all reagents shall conform to the specifications of the Committee on Analytical Reagents of the American Chemical Society, where such specifications are available. Other grades may be used, provided it is first ascertained that the reagent is of sufficiently high purity to permit its use without lessening the accuracy of the determination.

5.2 Reagent Water. Reagent water is interference free. All references to water in the method refer to reagent water unless otherwise specified.

5.3 Nitric Acid (concentrated), HNO_3.

5.4 Ammonium Hydroxide (concentrated), NH_4OH.

5.5 Silver Stock Standard Solution (1,000 mg/L), $AgNO_3$. Dissolve 0.7874 g anhydrous silver nitrate in water. Add 5 mL HNO_3 and bring to volume in a 500-mL volumetric flask (1 mL = 1 mg Ag). Alternatively, procure a certified aqueous standard from a supplier and verify by comparison with a second standard.

5.6 Silver working standards - These standards should be prepared from silver stock solution to be used as calibration standards at the time of analysis. These standards should be prepared with nitric acid and at the same concentrations as the analytical solution.

5.7 Iodine solution (1N). Dissolve 20 g potassium iodide (KI), in 50 mL of water. Add 12.7 g iodine (I_2) and dilute to 100 mL. Store in a brown bottle.

5.8 Cyanogen iodide solution. Add 4.0 mL ammonium hydroxide, 6.5 g potassium cyanide (KCN), and 5.0 mL of iodine solution to 50 mL of water. Mix and dilute to 100 mL with water. Do not keep longer than 2 weeks.

CAUTION: This reagent cannot be mixed with any acid solutions because toxic hydrogen cyanide will be produced.

5.9 Air.

5.10 Acetylene.

6.0 SAMPLE COLLECTION, PRESERVATION, AND HANDLING

6.1 All samples must have been collected using a sampling plan that addresses the considerations discussed in Chapter Nine of this manual.

6.2 All sample containers must be prewashed with detergents, acids, and reagent water. Plastic and glass containers are both suitable.

6.3 Aqueous samples must be acidified to a pH < 2 with nitric acid.

6.4 When possible, standards and samples should be stored in the dark and in brown bottles.

6.5 Nonaqueous samples shall be refrigerated, when possible, and analyzed as soon as possible.

7.0 PROCEDURE

7.1 Sample preparation - Aqueous samples should be prepared according to Steps 7.2 and 7.3. The applicability of a sample preparation technique to a new matrix type must be demonstrated by analyzing spiked samples and/or relevant standard reference materials.

7.2 Preparation of aqueous samples

7.2.1 Transfer a representative aliquot of the well-mixed sample to a beaker and add 3 mL of concentrated HNO_3. Cover the beaker with a ribbed watch glass. Place the beaker on a hot plate and cautiously evaporate to near dryness, making certain that the sample does not boil. DO NOT BAKE. Cool the beaker and add another 3-mL portion of concentrated HNO_3. Cover the beaker with a watch glass and return to the hot plate. Increase the temperature of the hot plate so that a gentle reflux action occurs.

NOTE: If the sample contains thiosulfates, this step may result in splatter of sample out of the beaker as the sample approaches dryness. This has been reported to occur with certain photographic types of samples.

7.2.2 Continue heating, adding additional acid, as necessary, until the digestion is complete (generally indicated when the digestate is light in color or does not change in appearance with continued refluxing). Again, evaporate to near dryness and cool the beaker. Add a small quantity of HNO_3 so that the final dilution contains 0.5% (v/v) HNO_3 and warm the beaker to dissolve any precipitate or residue resulting from evaporation.

7.2.3 Wash down the beaker walls and watch glass with water and, when necessary, filter the sample to remove silicates and other insoluble material that could clog the nebulizer. Adjust the volume to some predetermined value based on the expected metal concentrations. The sample is now ready for analysis.

7.3 If plating out of AgCl is suspected, the precipitate can be redissolved by adding cyanogen iodide to the sample. This can be done only after digestion and after neutralization of the sample to a pH > 7 to prevent formation of toxic cyanide under acid conditions. In this case do not adjust the sample volume to the predetermined value until the sample has been neutralized to pH > 7 and cyanogen iodide has been added. If cyanogen iodide addition to the sample is necessary, then the standards must be treated in the same manner. Cyanogen iodide must not be added to the acidified silver standards. New standards must be made, as directed in Steps 5.5 and 5.6, except that the acid addition step must be omitted. For example, to obtain a 100 mg/L working standard, transfer 10 mL of stock solution to a small beaker. Add water to make about 70 mL. Make the solution basic (pH above 7) with ammonium hydroxide. Rinse the pH meter electrodes into the solution with water. Add 1 mL cyanogen iodide and allow to stand 1 hour. Transfer quantitatively to a 100-mL volumetric flask and bring to volume with water.

CAUTION: CNI reagent can be added only after digestion to prevent formation of toxic cyanide under acidic conditions. CNI reagent must not be added to the acidified silver standards.

NOTE: Once the sample or sample aliquot has been treated with the CNI reagent and diluted per instruction, the solution has a cyanide concentration of approximately 260 mg/L. A solution of that cyanide concentration must be considered a potential hazardous waste and must be disposed of using an approved safety plan in accordance with local authority requirements. Until such time that a detailed disposal plan can be fully documented and approved, the use of the CNI reagent should be avoided.

7.4 The 328.1 nm wavelength line and background correction shall be employed.

7.5 An oxidizing air-acetylene flame shall be used.

7.6 Follow the manufacturer's operating instructions for all other spectrophotometer parameters.

8.0 QUALITY CONTROL

8.1 Refer to section 8.0 of Method 7000.

9.0 METHOD PERFORMANCE

9.1 Precision and accuracy data are available in Method 272.1 of "Methods for Chemical Analysis of Water and Wastes."

9.2 The data shown in Table 1 were obtained from records of state and contractor laboratories. The data are intended to show the precision of the combined sample preparation and analysis method.

10.0 REFERENCES

1. Methods for Chemical Analysis of Water and Wastes; U.S. Environmental Protection Agency. Office of Research and Development. Environmental Monitoring and Support Laboratory. ORD Publication Offices of Center for Environmental Research Information: Cincinnati, OH, 1983; EPA-600/4-79-020.

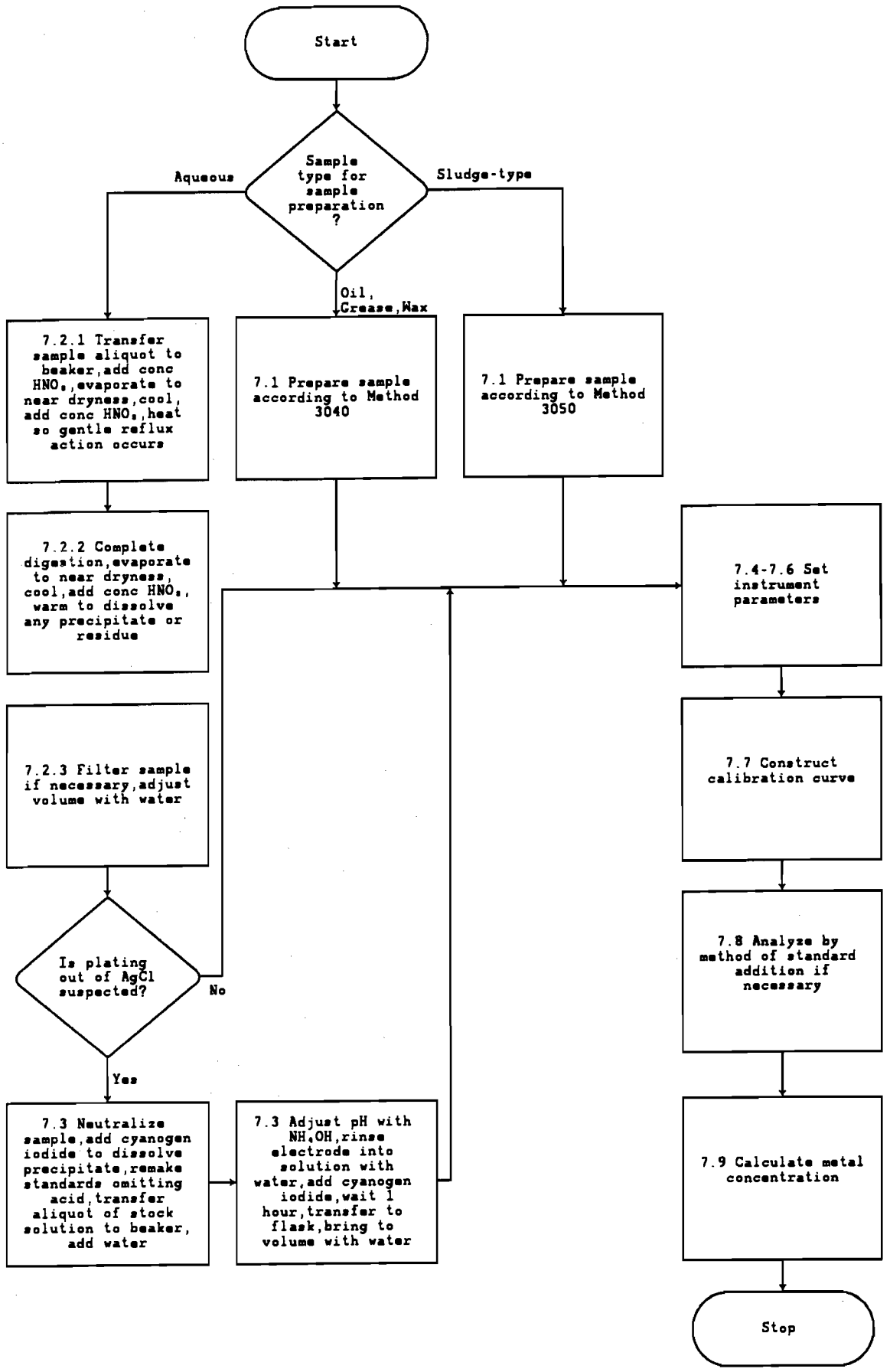
2. Gaskill, A., Compliation and Evaluation of RCRA Method Performance Data, Work Assignment No. 2, EPA Contract No. 68-01-7075, December 1987.

3. Rohrbough, W.G.; et al. Reagent Chemicals, American Chemical Society Specifications, 7th ed.; American Chemical Society: Washington, DC, 1986.

4. 1985 Annual Book of ASTM Standards, Vol. 11.01; "Standard Specification for Reagent Water"; ATSM: Philadelphia, PA, 1985; D1193-77.

TABLE 1.
METHOD PERFORMANCE DATA

Sample Matrix	Preparation Method	Laboratory Replicates
Wastewater treatment sludge	3050	2.3, 1.6 mg/Kg
Emission control dust	3050	1.8, 4.2 mg/Kg


Start
Sample type for sample preparation ?
Aqueous
Sludge-type
Oil, Grease, Wax
7.2.1 Transfer sample aliquot to beaker, add conc HNO3, evaporate to near dryness, cool, add conc HNO3, heat so gentle reflux action occurs
7.1 Prepare sample according to Method 3040
7.1 Prepare sample according to Method 3050
7.2.2 Complete digestion, evaporate to near dryness, cool, add conc HNO3, warm to dissolve any precipitate or residue
7.4-7.6 Set instrument parameters
7.2.3 Filter sample if necessary, adjust volume with water
7.7 Construct calibration curve
Is plating out of AgCl suspected?
No
Yes
7.8 Analyze by method of standard addition if necessary
7.3 Neutralize sample, add cyanogen iodide to dissolve precipitate, remake standards omitting acid, transfer aliquot of stock solution to beaker, add water
7.3 Adjust pH with NH4OH, rinse electrode into solution with water, add cyanogen iodide, wait 1 hour, transfer to flask, bring to volume with water
7.9 Calculate metal concentration
Stop

METHOD 7761

SILVER (ATOMIC ABSORPTION, FURNACE TECHNIQUE)

1.0 SCOPE AND APPLICATION

1.1 Method 7761 is an atomic absorption procedure approved for determining the concentration of silver in wastes, mobility procedure extracts, soils, and ground water. All samples must be subjected to an appropriate dissolution procedure.

2.0 SUMMARY OF METHOD

2.1 See Section 2.0 of Method 7000.

3.0 INTERFERENCES

3.1 See Section 3.0 of Method 7000 if interferences are suspected.

3.2 In addition to the normal interferences experienced during graphite furnace analysis, silver analysis can suffer from severe nonspecific absorption and light scattering caused by matrix components during atomization. Simultaneous background correction must be employed to avoid erroneously high results.

3.3 If the analyte is not completely volatilized and removed from the furnace during atomization, memory effects will occur. If this situation is detected, the tube should be cleaned by operating the furnace at higher atomization temperatures.

3.4 Silver nitrate solutions are light sensitive and have the tendency to plate out on container walls. Thus, silver standards should be stored in brown bottles.

3.5 Silver chloride is insoluble; therefore, hydrochloric acid should be avoided unless the silver is already in solution as a chloride complex.

4.0 APPARATUS AND MATERIALS

4.1 For basic apparatus, see Section 4.0 of Method 7000.

4.2 Instrument Parameters (General):

4.2.1 Drying Time and Temp: 30 sec at 125°C.

4.2.2 Ashing Time and Temp: 30 sec at 400°C.

4.2.3 Atomizing Time and Temp: 10 sec at 2700°C.

4.2.4 Purge Gas Atmosphere: Argon.

4.2.5 Wavelength: 328.1 nm.

4.2.6 Background Correction: Required.

4.2.7 Other operating parameters should be set as specified by the particular instrument manufacturer.

NOTE: The above concentration values and instrument conditions are for a Perkin-Elmer HGA-2100, based on the use of a 20 uL injection, continuous flow purge gas and non-pyrolytic graphite and are to be used as guidelines only. Smaller size furnace devices or those employing faster rates of atomization can be operated using lower atomization temperatures for shorter time periods than the above recommended settings.

5.0 REAGENTS

5.1 See Section 5.0 of Method 7000.

5.2 Silver Stock Standard Solution (1,000 mg/L), $AgNO_3$. Dissolve 0.7874 g anhydrous silver nitrate ($AgNO_3$), analytical reagent grade, water. Add 5 mL concentrated nitric acid (HNO_3) and bring to volume in a 500 mL volumetric flask (1 mL = 1 mg Ag). Alternatively, procure a certified standard from a supplier and verify by comparison with a second standard.

5.3 Silver working standards - These standards should be prepared with nitric acid such that the final acid concentration is 0.5% (v/v) HNO_3.

5.4 Ammonium hydroxide (concentrated), (NH_4OH). Base should be analyzed to determine levels of impurities. If impurities are detected, all analyses should be blank-corrected.

5.5 Iodine solution (1N). Dissolve 20 g potassium iodide (KI), analytical reagent grade, in 50 mL water. Add 12.7 g iodine (I_2), analytical reagent grade, and dilute to 100 mL with water. Store in a brown bottle.

5.6 Cyanogen iodide solution. To 50 mL water add 4.0 mL concentrated NH_4OH, 6.5 g potassium cyanide (KCN), and 5.0 mL of iodine solution. Mix and dilute to 100 mL with water. Do not keep longer than 2 weeks.

CAUTION: This reagent cannot be mixed with any acid solutions since highly toxic hydrogen cyanide will be produced.

6.0 SAMPLE COLLECTION, PRESERVATION, AND HANDLING

6.1 See Chapter Three, Step 3.1.3, Sample Handling and Preservation.

6.2 Standards and samples should be stored in the dark, in brown bottles, and refrigerated.

7.0 PROCEDURE

7.1 Sample preparation - Aqueous samples should be prepared according to Steps 7.2 and 7.3. The applicability of a sample preparation technique to a new matrix type must be demonstrated by analyzing spiked samples and/or relevant standard reference materials.

7.2 Preparation of aqueous samples

7.2.1 Transfer a representative aliquot of the well-mixed sample to a beaker and add 3 mL of concentrated HNO_3. Cover the beaker with a watch glass. Place the beaker on the hot plate and cautiously evaporate to near dryness, making certain that the sample does not boil. DO NOT BAKE. Cool the beaker and add another 3-mL portion of concentrated HNO_3. Cover the beaker with a watch glass and return to the hot plate. Increase the temperature of the hot plate so that a gentle reflux action occurs.

NOTE: If the sample contains thiosulfates, this step may result in splatter of sample out of the beaker as the sample approaches dryness. This has been reported to occur with certain types of photographic wastes.

7.2.2 Continue heating, adding additional acid, as necessary, until the digestion is complete (generally indicated when the digestate is light in color or does not change in appearance with continued refluxing). Again, evaporate to near dryness and cool the beaker. Add a small quantity of HNO_3 so that the final dilution contains 0.5% (v/v) HNO_3 and warm the beaker to dissolve any precipitate or residue resulting from evaporation.

7.2.3 Wash down the beaker walls and watch glass with water and, when necessary, filter the sample to remove silicates and other insoluble material that could clog the nebulizer. Adjust the volume to some predetermined value based on the expected metal concentrations. The sample is now ready for analysis.

7.3 If plating out of AgCl is suspected, the precipitate can be redissolved by adding cyanogen iodide to the sample. This can be done only after digestion and after neutralization of the sample to a pH > 7 to prevent formation of toxic cyanide under acid conditions. In this case, do not adjust the sample volume to the predetermined value until the sample has been neutralized to pH > 7 and cyanogen iodide has been added. If cyanogen iodide addition to the sample is necessary, then the standards must be treated in the same manner. Cyanogen iodide must not be added to the acidified silver standards. New standards must be made, as directed in Step 5.2, except that the acid addition step must be omitted. For example, to obtain a 100 mg/L working standard, transfer 10 mL of stock solution to a small beaker. Add water to make about 70 mL. Make the solution basic (pH above 7) with NH_4OH. Rinse the pH meter electrodes into the

solution with water. Add 1 mL cyanogen iodide and allow to stand 1 hour. Transfer quantitatively to a 100-mL volumetric flask and bring to volume with water.

CAUTION: CNI reagent can be added only after digestion to prevent formation of toxic cyanide under acidic conditions. CNI reagent must not be added to the acidified silver standards.

NOTE: Once the sample or sample aliquot has been treated with the CNI reagent and diluted per instruction, the solution has a cyanide concentration of approximately 260 mg/L. A solution of that cyanide concentration must be considered a potential hazardous waste and must be disposed of using an approved safety plan in accordance with local authority requirements. Until such time that a detailed disposal plan can be fully documented and approved, the use of the CNI reagent should be avoided.

7.4 The 328.1-nm wavelength line and background correction shall be used.

7.5 Following the manufacturer's operating instructions for all other spectrophotometer parameters.

7.6 Furnace parameters suggested by the manufacturer should be employed as guidelines. Since temperature-sensing mechanisms and temperature controllers can vary between instruments or with time, the validity of the furnace parameters must be periodically confirmed by systematically altering the furnace parameters while analyzing a standard. In this manner, losses of analyte due to higher than necessary temperature settings or losses in sensitivity due to less than optimum settings can be minimized. Similar verification of furnace parameters may be required for complex sample matrices.

7.7 Inject a measured uL aliquot of sample into the furnace and atomize. If the concentration found is greater than the highest standard, the sample should be diluted in the same acid matrix and reanalyzed. The use of multiple injections can improve accuracy and help detect furnace pipetting errors.

7.8 Either (1) run a series of silver standards and construct a calibration curve by plotting the concentrations of the standards against the absorbances or (2) for the method of standard additions, plot added concentration versus abosrbance. For instruments that read directly in concentration, set the curve corrector to read out the proper concentration.

7.9 Analyze, by the method of standard additions, all EP extracts, all samples analyzed as part of a delisting petition, and all samples that suffer from matrix interferences.

7.10 Calculate metal concentrations by (1) the method of standard additions, or (2) from a calibration curve, or (3) directly from the instrument's concentration readout. All dilution or concentration factors must be taken into account. Concentrations reported for multiphased samples must be appropriately qualified.

8.0 QUALITY CONTROL

8.1 All quality control data should be maintained and available for easy reference or inspection.

8.2 Calibration curves must be composed of a minimum of a calibration blank and three standards. A calibration curve must be prepared each day.

8.3 Dilute samples if they are more concentrated than the highest standard or if they fall on the plateau of a calibration curve.

8.4 Employ a minimum of one reagent blank per sample batch or every 20 samples to determine if contamination or any memory effects are occurring.

8.5 Verify calibration with an independently prepared quality control reference sample every 10 samples.

8.6 Run one spiked replicate sample for every 10 samples or per analytical batch, whichever is more frequent. A replicate sample is a sample brought through the entire sample preparation process.

8.7 Duplicates, spiked samples, and check standards should be routinely analyzed. Refer to Chapter One for the proper protocol.

8.8 The method of standard additions (see Method 7000, Step 8.7) shall be used for the analysis of all EP extracts, on all analyses submitted as part of a delisting petition, and whenever a new sample matrix is being analyzed.

9.0 METHOD PERFORMANCE

9.1 Precision and accuracy data are available in Method 272.2 of Methods for Chemical Analysis of Water and Wastes.

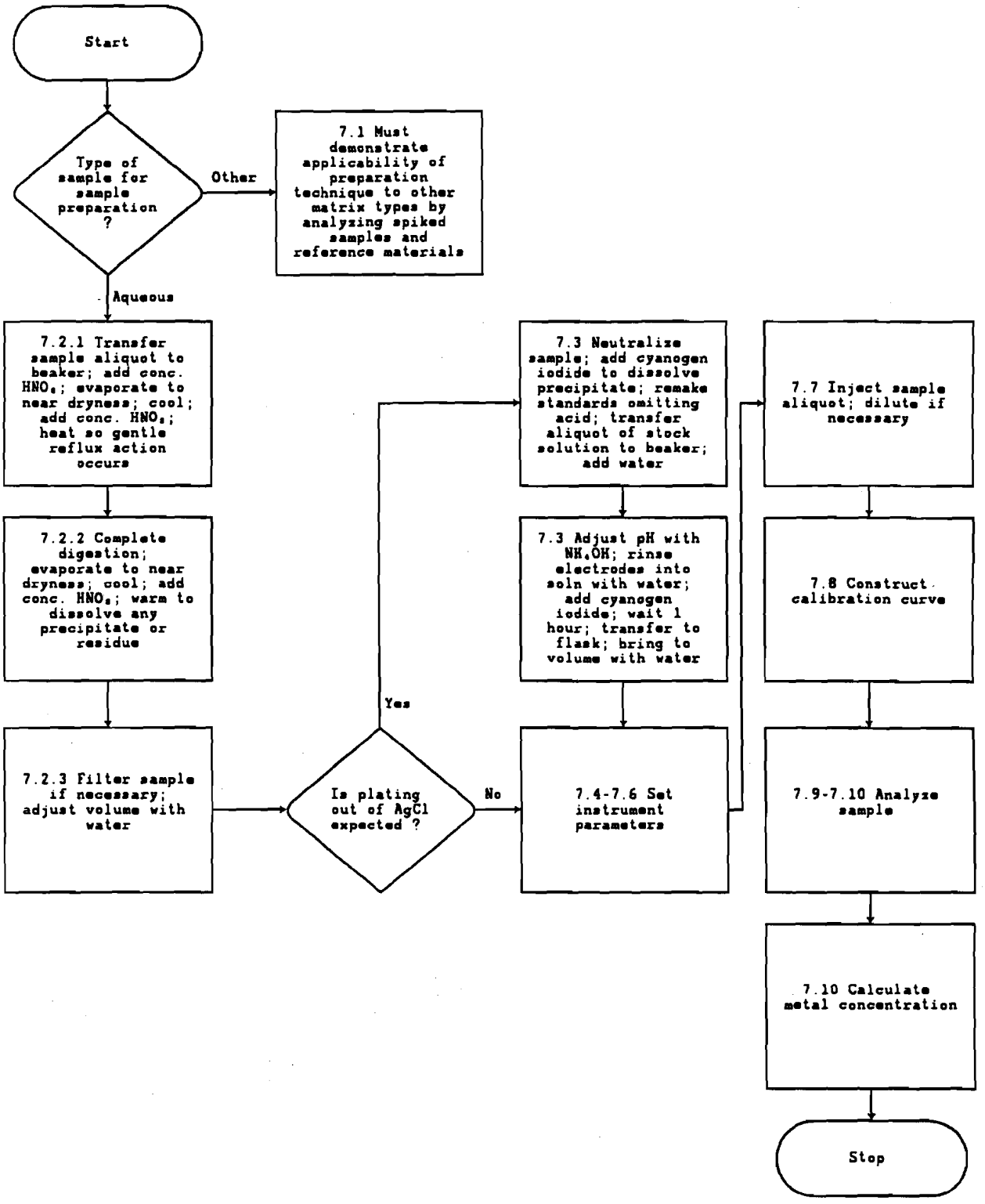
9.2 The performance characteristics for an aqueous sample free of interferences are:

Optimum concentration range: 1-25 ug/L.
Detection limit: 0.2 ug/L.

10.0 REFERENCES

1. Methods for Chemical Analysis of Water and Wastes; U.S. Environmental Protection Agency. Office of Research and Development. Environmental Monitoring and Support Laboratory. ORD Publication Offices of Center for Environmental Research Information: Cincinnati, OH, 1983; EPA-600/4-79-020.

METHOD 7761
SILVER (ATOMIC ABSORPTION, FURNACE TECHNIQUE)



METHOD 7770

SODIUM (ATOMIC ABSORPTION, DIRECT ASPIRATION)

1.0 SCOPE AND APPLICATION

1.1 See Section 1.0 of Method 7000.

2.0 SUMMARY OF METHOD

2.1 See Section 2.0 of Method 7000.

3.0 INTERFERENCES

3.1 See Section 3.0 of Method 7000 if interferences are suspected.

3.2 Ionization interferences can affect analysis for sodium; therefore, samples and standards must be matrix matched or an ionization suppressant employed.

3.3 Sodium is a universal contaminant, and great care should be taken to avoid contamination.

4.0 APPARATUS AND MATERIALS

4.1 For basic apparatus, see Section 4.0 of Method 7000.

4.2 Instrument parameters (general):

4.2.1 **Sodium hollow cathode lamp.**
4.2.2 **Wavelength:** 589.6 nm.
4.2.3 **Fuel:** Acetylene.
4.2.4 **Oxidant:** Air.
4.2.5 **Type of flame:** Oxidizing (fuel lean).
4.2.6 **Background correction:** Not required.

5.0 REAGENTS

5.1 See Section 5.0 of Method 7000.

5.2 Preparation of standards:

5.2.1 **Stock solution:** Dissolve 2.542 g sodium chloride, NaCl (analytical reagent grade), in Type II water, acidify with 10 mL redistilled HNO_3, and dilute to 1 liter with Type II water. Alternatively, procure a certified standard from a supplier and verify by comparison with a second standard.

5.2.2 Prepare dilutions of the stock solution to be used as calibration standards at the time of analysis. The calibration standards should be prepared using the same type of acid and at the same concentration as will result in the sample to be analyzed after processing.

6.0 SAMPLE COLLECTION, PRESERVATION, AND HANDLING

6.1 See Chapter Three, Section 3.1.3, Sample Handling and Preservation.

7.0 PROCEDURE

7.1 Sample preparation: The procedures for preparation of the sample are given in Chapter Three, Section 3.2.

7.2 See Method 7000, Paragraph 7.2, Direct Aspiration.

8.0 QUALITY CONTROL

8.1 See Section 8.0 of Method 7000.

9.0 METHOD PERFORMANCE

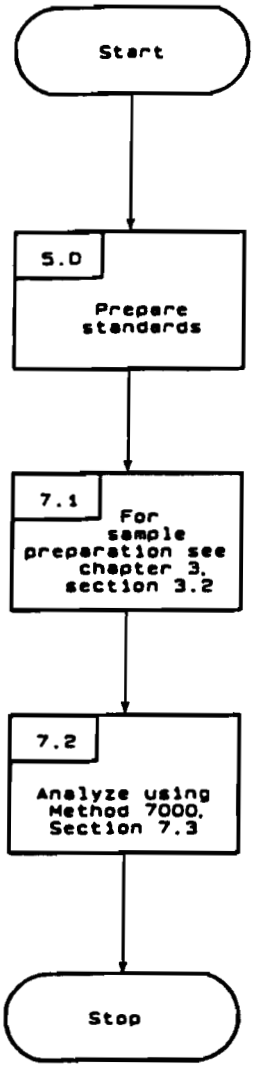
9.1 The performance characteristics for an aqueous sample free of interferences are:

Optimum concentration range: 0.03-1 mg/L with a wavelength of 589.6 nm.
Sensitivity: 0.015 mg/L.
Detection limit: 0.002 mg/L.

9.2 In a single laboratory, analysis of a mixed industrial-domestic waste effluent, digested with Method 3010, at concentrations of 8.2 and 52 mg/L gave standard deviations of $\pm$0.1 and $\pm$0.8, respectively. Recoveries at these levels were 102% and 100%, respectively.

10.0 REFERENCES

1. Methods for Chemical Analysis of Water and Wastes, EPA-600/4-82-055, December 1982, Method 273.1.


Start
5.0
Prepare standards
7.1
For sample preparation see chapter 3, section 3.2
7.2
Analyze using Method 7000, Section 7.3
Stop

METHOD 7780

STRONTIUM (ATOMIC ABSORPTION, DIRECT ASPIRATION)

1.0 SCOPE AND APPLICATION

1.1 See Section 1.0 of Method 7000.

2.0 SUMMARY OF METHOD

2.1 See Section 2.0 of Method 7000.

3.0 INTERFERENCES

3.1 See Section 3.0 of Method 7000.

3.2 Chemical interference caused by silicon, aluminum, and phosphate are controlled by adding lanthanum chloride. Potassium chloride is added to suppress the ionization of strontium. All samples and standards should contain 1 mL of lanthanum chloride/potassium chloride solution (Step 5.3) per 10 mL of solution.

4.0 APPARATUS AND MATERIALS

4.1 For basic apparatus, see Section 4.0 of Method 7000.

4.2 Instrument parameters (general):

4.2.1 Strontium hollow cathode lamp.

4.2.2 Wavelength: 460.7 nm.

4.2.3 Fuel: Acetylene.

4.2.4 Oxidant: Air.

4.2.5 Type of flame: Oxidizing (fuel lean).

4.2.6 Background correction: not required.

5.0 REAGENTS

5.1 See Section 5.0 of Method 7000.

5.2 Preparation of standards

5.2.1 Stock solution: (1.0 mL = 1.0 mg Sr). Dissolve 2.415 g of strontium nitrate, $Sr(NO_3)_2$, in 10 mL of concentrated HCl and 700 mL of water. Dilute to 1 liter with water. Alternatively, procure a certified standard from a supplier and verify by comparison with a second standard.

5.2.2 Prepare dilutions of the stock solution to be used as calibration standards at the time of analysis. The calibration standards should be prepared using the same type of acid as the samples and cover the range of expected concentrations in the samples. Calibration standards should also contain 1 mL of lanthanum chloride/potassium chloride solution per 10 mL.

5.3 Lanthanum Chloride/Potassium Chloride Solution. Dissolve 11.73 g of lanthanum oxide, La_2O_3, in a minimum amount of concentrated hydrochloric acid (approximately 50 mL). Add 1.91 g of potassium chloride, KCl. Allow solution to cool to room temperature and dilute to 100 mL with water.

CAUTION: REACTION IS VIOLENT! Add acid slowly and in small portions to control the reaction rate upon mixing.

6.0 SAMPLE COLLECTION, PRESERVATION, AND HANDLING

6.1 See Chapter Three, Step 3.1.3, Sample Handling and Preservation.

7.0 PROCEDURE

7.1 Sample preparation - The procedures for preparation of the sample are given in Chapter Three, Step 3.2.

7.2 See Method 7000, Step 7.2, Direct Aspiration.

8.0 QUALITY CONTROL

8.1 See Section 8.0 of Method 7000.

9.0 METHOD PERFORMANCE

9.1 The performance characteristics for an aqueous sample free of interferences are:

Optimum concentration range: 0.3 - 5 mg/L at a wavelength of 460.7 nm.
Sensitivity: 0.15 mg/L.
Detection limit: 0.03 mg/L.

9.1.1 Recoveries of known amounts of strontium in a series of prepared standards were as given in Table 1.

10.0 REFERENCES

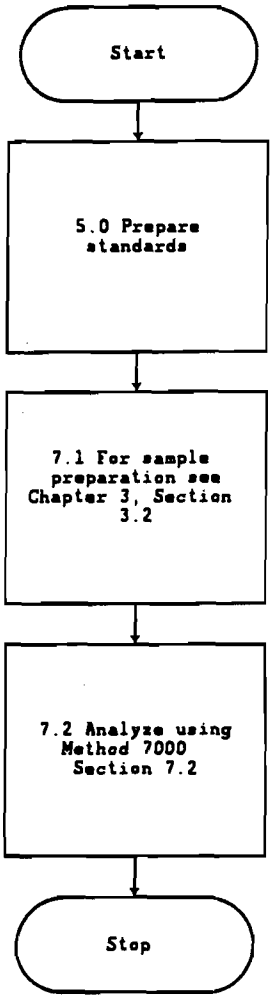
1. Annual Book of ASTM Standards; ASTM: Philadelphia, PA, 1983; D3920.

TABLE 1.
RECOVERY

Amount added, mg/L	Amount found, mg/L	Bias	% Bias	Significant (95 % confidence level)
		Reagent Water Type II		
1.00	0.998	-0.002	-0.2	no
0.50	0.503	+0.003	+0.6	no
0.10	0.102	+0.002	+2	no
		Water of Choice		
1.00	1.03	+0.03	+ 3	no
0.50	0.504	+0.004	+ 0.8	no
0.10	0.086	-0.014	-14	no

Reference: Annual Book of ASTM Standards; ASTM: Philadelphia, PA, 1983; D3920.

METHOD 7780
STRONTIUM (ATOMIC ABSORPTION, DIRECT ASPIRATION)



METHOD 7840

THALLIUM (ATOMIC ABSORPTION, DIRECT ASPIRATION)

1.0 SCOPE AND APPLICATION

1.1 See Section 1.0 of Method 7000.

2.0 SUMMARY OF METHOD

2.1 See Section 2.0 of Method 7000.

3.0 INTERFERENCES

3.1 See Section 3.0 of Method 7000 if interferences are suspected.

3.2 Background correction is required.

3.3 Hydrochloric acid should not be used.

4.0 APPARATUS AND MATERIALS

4.1 For basic apparatus, see Section 4.0 of Method 7000.

4.2 Instrument parameters (general):

4.2.1 **Thallium hollow cathode lamp.**
4.2.2 **Wavelength:** 276.8 nm.
4.2.3 **Fuel:** Acetylene.
4.2.4 **Oxidant:** Air.
4.2.5 **Type of flame:** Oxidizing (fuel lean).
4.2.6 **Background correction:** Required.

5.0 REAGENTS

5.1 See Section 5.0 of Method 7000.

5.2 Preparation of standards:

5.2.1 **Stock solution:** Dissolve 1.303 g thallium nitrate, $TlNO_3$ (analytical reagent grade), in Type II water, acidify with 10 mL concentrated HNO_3, and dilute to 1 liter with Type II water. Alternatively, procure a certified standard from a supplier and verify by comparison with a second standard.

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5.2.2 Prepare dilutions of the stock solution to be used as calibration standards at the time of analysis. The calibration standards should be prepared using the same type of acid and at the same concentration as will result in the sample to be analyzed after processing (0.5% v/v HNO_3).

6.0 SAMPLE COLLECTION, PRESERVATION, AND HANDLING

6.1 See Chapter Three, Section 3.1.3, Sample Handling and Preservation.

7.0 PROCEDURE

7.1 Sample preparation: The procedures for preparation of the sample are given in Chapter Three, Section 3.2.

7.2 See Method 7000, Paragraph 7.2, Direct Aspiration.

8.0 QUALITY CONTROL

8.1 See Section 8.0 of Method 7000.

9.0 METHOD PERFORMANCE

9.1 The performance characteristics for an aqueous sample free of interferences are:

Optimum concentration range: 1-20 mg/L with a wavelength of 276.8 nm.
Sensitivity: 0.5 mg/L.
Detection limit: 0.1 mg/L.

9.2 In a single laboratory, analysis of a mixed industrial-domestic waste effluent, digested with Method 3010, at concentrations of 0.6, 3, and 15 mg/L gave standard deviations of $\pm$0.018, $\pm$0.05, and $\pm$0.2, respectively. Recoveries at these levels were 100%, 98%, and 98%, respectively.

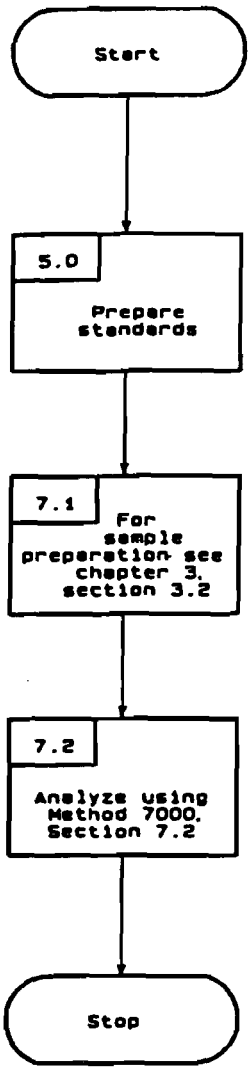
9.3 For concentrations of thallium below 0.2 mg/L, the furnace technique (Method 7841) is recommended.

10.0 REFERENCES

1. Methods for Chemical Analysis of Water and Wastes, EPA-600/4-82-055, December 1982, Method 279.1.

METHOD 7840

THALLIUM (ATOMIC ABSORPTION, DIRECT ASPIRATION)



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METHOD 7841

THALLIUM (ATOMIC ABSORPTION, FURNACE TECHNIQUE)

1.0 SCOPE AND APPLICATION

1.1 See Section 1.0 of Method 7000.

2.0 SUMMARY OF METHOD

2.1 See Section 2.0 of Method 7000.

3.0 INTERFERENCES

3.1 See Section 3.0 of Method 7000 if interferences are suspected.

3.2 Background correction is required.

3.3 Hydrochloric acid or excessive chloride will cause volatilization of thallium at low temperatures. Verification that losses are not occurring, by spiked samples or standard additions, must be made for each sample matrix.

3.4 Palladium is a suitable matrix modifier for thallium analysis.

4.0 APPARATUS AND MATERIALS

4.1 For basic apparatus, see Section 4.0 of Method 7000.

4.2 Instrument parameters (general):

4.2.1 **Drying time and temp:** 30 sec at 125°C.
4.2.2 **Ashing time and temp:** 30 sec at 400°C.
4.2.3 **Atomizing time and temp:** 10 sec at 2400°C.
4.2.4 **Purge gas:** Argon or nitrogen.
4.2.5 **Wavelength:** 276.8 nm.
4.2.6 **Background correction:** Required.
4.2.7 Other operating parameters should be set as specified by the particular instrument manufacturer.

NOTE: The above concentration values and instrument conditions are for a Perkin-Elmer HGA-2100, based on the use of a 20-uL injection, continuous-flow purge gas, and nonpyrolytic graphite. Smaller sizes of furnace devices or those employing faster rates of atomization can be operated using lower atomization temperatures for shorter time periods than the above-recommended settings.

5.0 REAGENTS

5.1 See Section 5.0 of Method 7000.

5.2 Preparation of standards:

5.2.1 Stock solution: Dissolve 1.303 g thallium nitrate, $TlNO_3$ (analytical reagent grade), in Type II water, acidify with 10 mL concentrated HNO_3, and dilute to 1 liter with Type II water. Alternatively, procure a certified standard from a supplier and verify by comparison with a second standard.

5.2.2 Prepare dilutions of the stock solution to be used as calibration standards at the time of analysis. The calibration standards should be prepared using the same type of acid and at the same concentrations as in the sample after processing (0.5% v/v HNO_3).

5.3 Palladium chloride: Weigh 0.25 g of $PdCl_2$ to the nearest 0.0001 g. Dissolve in 10 mL of 1:1 HNO_3 and dilute to 1 liter with Type II water. Use equal volumes of sample and palladium solution.

6.0 SAMPLE COLLECTION, PRESERVATION, AND HANDLING

6.1 See Chapter Three, Section 3.1.3, Sample Handling and Preservation.

7.0 PROCEDURE

7.1 Sample preparation: The procedures for preparation of the sample are given in Chapter Three, Section 3.2.

7.2 See Method 7000, Paragraph 7.3, Furnace Procedure. The calculation is given in Method 7000, Paragraph 7.4.

8.0 QUALITY CONTROL

8.1 See Section 8.0 of Method 7000.

9.0 METHOD PERFORMANCE

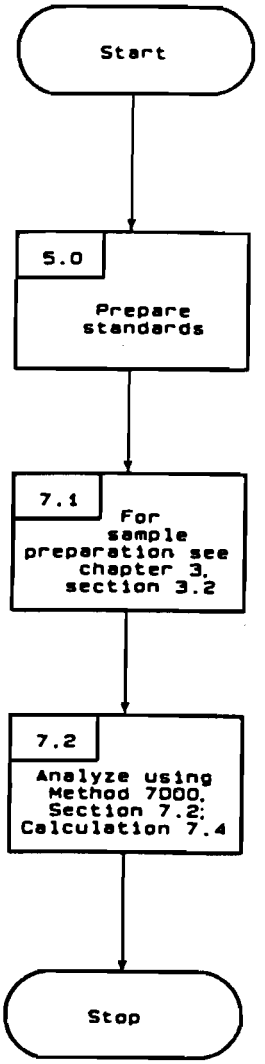
9.1 Precision and accuracy data are not available at this time.

9.2 The performance characteristics for an aqueous sample free of interferences are:

Optimum concentration range: 5-100 ug/L.
Detection limit: 1 ug/L.

10.0 REFERENCES

1. Application of Matrix-Modification in Determination of Thallium in Wastewater by Graphite-Furnace Atomic-Absorption Spectrometry, Talanta, 31(2) (1984), pp. 150-152.


Start
5.0
Prepare standards
7.1
For sample preparation see chapter 3, section 3.2
7.2
Analyze using Method 7000, Section 7.2; Calculation 7.4
Stop

METHOD 7870

TIN (ATOMIC ABSORPTION, DIRECT ASPIRATION)

1.0 SCOPE AND APPLICATION

1.1 See Section 1.0 of Method 7000.

2.0 SUMMARY OF METHOD

2.1 See Section 2.0 of Method 7000.

3.0 INTERFERENCES

3.1 See Section 3.0 of Method 7000 if interferences are suspected.

4.0 APPARATUS AND MATERIALS

4.1 For basic apparatus, see Section 4.0 of Method 7000.

4.2 Instrument parameters (general):

4.2.1 **Tin hollow cathode lamp.**
4.2.2 **Wavelength:** 286.3 nm.
4.2.3 **Fuel:** Acetylene.
4.2.4 **Oxidant:** Nitrous oxide.
4.2.5 **Type of flame:** Fuel rich.
4.2.6 **Background correction:** Not required.

5.0 REAGENTS

5.1 See Section 5.0 of Method 7000.

5.2 Preparation of standards:

5.2.1 **Stock solution:** Dissolve 1.000 g of tin metal (analytical reagent grade) in 100 mL of concentrated HCl and dilute to 1 liter with Type II water. Alternatively, procure a certified standard from a supplier and verify by comparison with a second standard.

5.2.2 Prepare dilutions of the stock solution to be used as calibration standards at the time of analysis. The calibration standards should be prepared using the same type of acid and at the same concentration as will result in the sample to be analyzed after processing.

6.0 SAMPLE COLLECTION, PRESERVATION, AND HANDLING

6.1 See Chapter Three, Section 3.1.3, Sample Handling and Preservation.

7.0 PROCEDURE

7.1 Sample preparation: The procedures for preparation of the sample are given in Chapter Three, Section 3.2.

7.2 See Method 7000, Paragraph 7.2, Direct Aspiration.

8.0 QUALITY CONTROL

8.1 See Section 8.0 of Method 7000.

9.0 METHOD PERFORMANCE

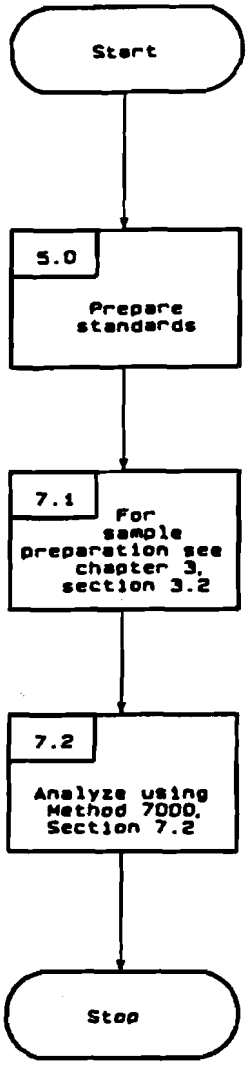
9.1 The performance characteristics for an aqueous sample free of interferences are:

Optimum concentration range: 10-300 mg/L with a wavelength of 286.3 nm.
Sensitivity: 4 mg/L.
Detection limit: 0.8 mg/L.

9.2 In a single laboratory, analysis of a mixed industrial-domestic waste effluent, digested with Method 3010, at concentrations of 4, 20, and 60 mg/L gave standard deviations of ±0.25, ±0.5, and ±0.5, respectively. Recoveries at these levels were 96%, 101%, and 101%, respectively.

10.0 REFERENCES

1. Methods for Chemical Analysis of Water and Wastes, EPA-600/4-82-055, December 1982, Method 282.1.


Start
5.0
Prepare standards
7.1
For sample preparation see chapter 3, section 3.2
7.2
Analyze using Method 7000, Section 7.2
Stop

METHOD 7910

VANADIUM (ATOMIC ABSORPTION, DIRECT ASPIRATION)

1.0 SCOPE AND APPLICATION

1.1 See Section 1.0 of Method 7000.

2.0 SUMMARY OF METHOD

2.1 See Section 2.0 of Method 7000.

3.0 INTERFERENCES

3.1 See Section 3.0 of Method 7000 if interferences are suspected.

3.2 Background correction may be required.

3.3 High concentrations of aluminum or titanium, or the presence of Bi, Cr, Co, Fe, acetic acid, phosphoric acid, surfactants, detergents, or alkali metals, may interfere. The interference can be controlled by adding 1,000 mg/L aluminum to samples and standards.

4.0 APPARATUS AND MATERIALS

4.1 For basic apparatus, see Section 4.0 of Method 7000.

4.2 Instrument parameters (general):

4.2.1 **Vanadium hollow cathode lamp.**
4.2.2 **Wavelength:** 318.4 nm.
4.2.3 **Fuel:** Acetylene.
4.2.4 **Oxidant:** Nitrous oxide.
4.2.5 **Type of flame:** Fuel rich.
4.2.6 **Background correction:** Required.

5.0 REAGENTS

5.1 See Section 5.0 of Method 7000.

5.2 Preparation of standards:

5.2.1 **Stock solution:** Dissolve 1.7854 g of vanadium pentoxide, V_2O_5 (analytical reagent grade), in 10 mL of concentrated nitric acid and dilute to 1 liter with Type II water. Alternatively, procure a certified standard from a supplier and verify by comparison with a second standard.

5.2.2 Prepare dilutions of the stock solution to be used as calibration standards at the time of analysis. The calibration standards should be prepared using the same type of acid and at the same concentration as will result in the sample to be analyzed after processing. In addition, 2 mL of the aluminum nitrate solution described in Paragraph 5.2.3 should be added to each 100 mL of standards and samples.

5.2.3 **Aluminum nitrate solution:** Dissolve 139 g aluminum nitrate ($Al[NO_3]_3 \cdot 9H_2O$) in 150 mL Type II water; heat to complete dissolution. Allow to cool and dilute to 200 mL with Type II water. All samples and standards should contain 2 mL of this solution per 100 mL.

6.0 SAMPLE COLLECTION, PRESERVATION, AND HANDLING

6.1 See Chapter Three, Section 3.1.3, Sample Handling and Preservation.

7.0 PROCEDURE

7.1 Sample preparation: The procedures for preparation of the sample are given in Chapter Three, Section 3.2.

7.2 See Method 7000, Paragraph 7.2, Direct Aspiration.

8.0 QUALITY CONTROL

8.1 See Section 8.0 of Method 7000.

9.0 METHOD PERFORMANCE

9.1 The performance characteristics for an aqueous sample free of interferences are:

Optimum concentration range: 2-100 mg/L with a wavelength of 318.4 nm.
Sensitivity: 0.8 mg/L.
Detection limit: 0.2 mg/L.

9.2 In a single laboratory), analysis of a mixed industrial-domestic waste effluent, digested with Method 3010, at concentrations of 2, 10, and 50 mg/L gave standard deviations of ±0.1, ±0.1, and ±0.2, respectively. Recoveries at these levels were 100%, 95%, and 97%, respectively.

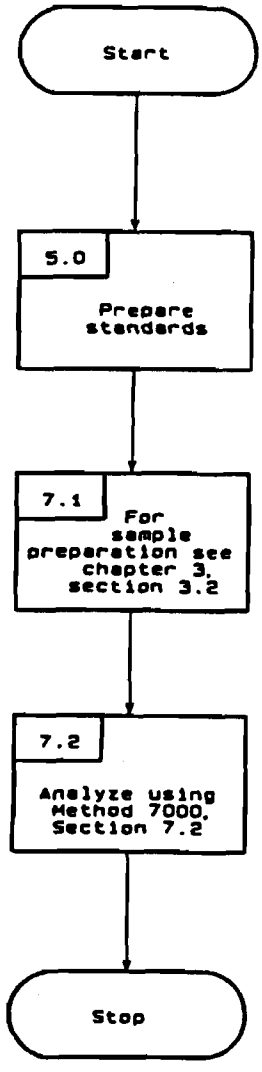
9.3 For concentrations of vanadium below 0.5 mg/L, the furnace technique (Method 7911) is recommended.

10.0 REFERENCES

1. Methods for Chemical Analysis of Water and Wastes, EPA-600/4-82-055, December 1982, Method 286.1.

METHOD 7910

VANADIUM (ATOMIC ABSORPTION, DIRECT ASPIRATION)



METHOD 7911

VANADIUM (ATOMIC ABSORPTION, FURNACE TECHNIQUE)

1.0 SCOPE AND APPLICATION

1.1 See Section 1.0 of Method 7000.

2.0 SUMMARY OF METHOD

2.1 See Section 2.0 of Method 7000.

3.0 INTERFERENCES

3.1 See Section 3.0 of Method 7000 if interferences are suspected.

3.2 Background correction is required.

3.3 Vanadium is refractory and prone to form carbides. Consequently, memory effects are common, and care should be taken to clean the furnace before and after analysis.

3.4 Nitrogen should not be used as a purge gas.

4.0 APPARATUS AND MATERIALS

4.1 For basic apparatus, see Section 4.0 of Method 7000.

4.2 Instrument parameters (general):

4.2.1 **Drying time and temp:** 30 sec at 125°C.
4.2.2 **Ashing time and temp:** 30 sec at 1400°C.
4.2.3 **Atomizing time and temp:** 15 sec at 2800°C.
4.2.4 **Purge gas:** Argon (nitrogen should not be used).
4.2.5 **Wavelength:** 318.4 nm.
4.2.6 **Background correction:** Required.
4.2.7 Other operating parameters should be set as specified by the particular instrument manufacturer.

NOTE: The above concentration values and instrument conditions are for a Perkin-Elmer HGA-2100, based on the use of a 20-uL injection, continuous-flow purge gas, and nonpyrolytic graphite. Smaller sizes of furnace devices or those employing faster rates of atomization can be operated using lower atomization temperatures for shorter time periods than the above-recommended settings.

5.0 REAGENTS

5.1 See Section 5.0 of Method 7000.

5.2 Preparation of standards:

5.2.1 Stock solution: Dissolve 1.7854 g of vanadium pentoxide, V_2O_5 (analytical reagent grade), in 10 mL of concentrated nitric acid and dilute to 1 liter with Type II water. Alternatively, procure a certified standard from a supplier and verify by comparison with a second standard.

5.2.2 Prepare dilutions of the stock solution to be used as calibration standards at the time of analysis. The calibration standards should be prepared using the same type of acid and at the same concentrations as in the sample after processing (0.5% v/v HNO_3).

6.0 SAMPLE COLLECTION, PRESERVATION, AND HANDLING

6.1 See Chapter Three, Section 3.1.3, Sample Handling and Preservation.

7.0 PROCEDURE

7.1 Sample preparation: The procedures for preparation of the sample are given in Chapter Three, Section 3.2.

7.2 See Method 7000, Paragraph 7.3, Furnace Procedure. The calculation is given in Method 7000, Paragraph 7.4.

8.0 QUALITY CONTROL

8.1 See Section 8.0 of Method 7000.

9.0 METHOD PERFORMANCE

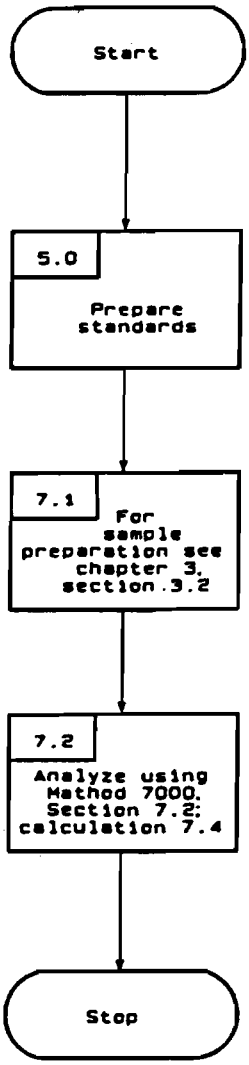
9.1 Precision and accuracy data are available in Method 286.2 of Methods for Chemical Analysis of Water and Wastes.

9.2 The performance characteristics for an aqueous sample free of interferences are:

Optimum concentration range: 10-200 ug/L.
Detection limit: 4 ug/L.

10.0 REFERENCES

1. Methods for Chemical Analysis of Water and Wastes, EPA-600/4-82-055, December 1982, Method 286.2.


Start
5.0
Prepare standards
7.1
For sample preparation see chapter 3, section 3.2
7.2
Analyze using Method 7000, Section 7.2; calculation 7.4
Stop

METHOD 7950

ZINC (ATOMIC ABSORPTION, DIRECT ASPIRATION)

1.0 SCOPE AND APPLICATION

1.1 See Section 1.0 of Method 7000.

2.0 SUMMARY OF METHOD

2.1 See Section 2.0 of Method 7000.

3.0 INTERFERENCES

3.1 See Section 3.0 of Method 7000 if interferences are suspected.

3.2 High levels of silicon, copper, or phosphate may interfere. Addition of strontium (1,500 mg/L) removes the copper and phosphate interference.

3.3 Zinc is a universal contaminant, and great care should be taken to avoid contamination.

4.0 APPARATUS AND MATERIALS

4.1 For basic apparatus, see Section 4.0 of Method 7000.

4.2 Instrument parameters (general):

4.2.1 **Zinc hollow cathode lamp.**
4.2.2 **Wavelength:** 213.9 nm.
4.2.3 **Fuel:** Acetylene.
4.2.4 **Oxidant:** Air.
4.2.5 **Type of flame:** Oxidizing (fuel lean).
4.2.6 **Background correction:** Required.

5.0 REAGENTS

5.1 See Section 5.0 of Method 7000.

5.2 Preparation of standards:

5.2.1 **Stock solution:** Dissolve 1.000 g zinc metal (analytical reagent grade) in 10 mL of concentrated nitric acid and dilute to 1 liter with Type II water. Alternatively, procure a certified standard from a supplier and verify by comparison with a second standard.

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5.2.2 Prepare dilutions of the stock solution to be used as calibration standards at the time of analysis. The calibration standards should be prepared using the same type of acid and at the same concentration as will result in the sample to be analyzed after processing.

6.0 SAMPLE COLLECTION, PRESERVATION, AND HANDLING

6.1 See Chapter Three, Section 3.1.3, Sample Handling and Preservation.

7.0 PROCEDURE

7.1 Sample preparation: The procedures for preparation of the sample are given in Chapter Three, Section 3.2.

7.2 See Method 7000, Paragraph 7.2, Direct Aspiration.

8.0 QUALITY CONTROL

8.1 See Section 8.0 of Method 7000.

9.0 METHOD PERFORMANCE

9.1 The performance characteristics for an aqueous sample free of interferences are:

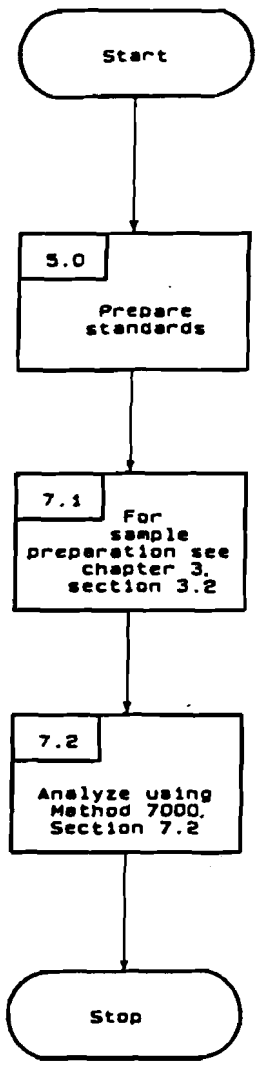
Optimum concentration range: 0.05-1 mg/L with a wavelength of 213.9 nm.
Sensitivity: 0.02 mg/L.
Detection limit: 0.005 mg/L.

9.2 For concentrations of zinc below 0.01 mg/L, the furnace technique (Method 7951) is recommended.

9.3 Precision and accuracy data are available in Method 289.1 of Methods for Chemical Analysis of Water and Wastes.

10.0 REFERENCES

1. Methods for Chemical Analysis of Water and Wastes, EPA-600/4-82-055, December 1982, Method 289.1.


Start
5.0
Prepare standards
7.1
For sample preperation see chapter 3, section 3.2
7.2
Analyze using Method 7000, Section 7.2
Stop

METHOD 7951

ZINC (ATOMIC ABSORPTION, FURNACE TECHNIQUE)

1.0 SCOPE AND APPLICATION

1.1 See Section 1.0 of Method 7000.

2.0 SUMMARY OF METHOD

2.1 See Section 2.0 of Method 7000.

3.0 INTERFERENCES

3.1 See Section 3.0 of Method 7000.

3.2 Background correction should be used.

3.3 Zinc is a universal contaminant. Because of this and the high sensitivity of this method, great care should be taken to avoid contamination.

4.0 APPARATUS AND MATERIALS

4.1 For basic apparatus, see Section 4.0 of Method 7000.

4.2 Instrument parameters (general):

4.2.1 Drying time and temp: 30 sec at 125°C.

4.2.2 Ashing time and temp: 30 sec at 400°C.

4.2.3 Atomizing time and temp: 10 sec at 2500°C.

4.2.4 Purge gas: Argon or nitrogen.

4.2.5 Wavelength: 213.9 nm.

4.2.6 Background correction: Required.

4.2.7 Other operating parameters should be set as specified by the particular instrument manufacturer.

NOTE: The above concentration values and instrument conditions are for a Perkin-Elmer HGA-2100, based on the use of a 20-uL injection, continuous-flow purge gas, and nonpyrolytic graphite. Smaller size furnace devices or those employing faster rates of atomization can be operated using lower

atomization temperatures for shorter time periods than the above-recommended settings.

5.0 REAGENTS

5.1 See Section 5.0 of Method 7000.

5.2 Preparation of standards

5.2.1 Stock solution - Dissolve 1.000 g zinc metal (analytical reagent grade) in 10 mL of concentrated nitric acid and dilute to 1 liter with water. Alternatively, procure a certified standard from a supplier and verify by comparison with a second standard.

5.2.2 Prepare dilutions of the stock solution to be used as calibration standards at the time of analysis. The calibration standards should be prepared using the same type of acid and at the same concentrations as in the sample after processing (0.5% v/v HNO_3).

6.0 SAMPLE COLLECTION, PRESERVATION, AND HANDLING

6.1 See Chapter Three, Step 3.1.3, Sample Handling and Preservation.

7.0 PROCEDURE

7.1 Sample Preparation - The procedures for preparation of the sample are given in Chapter Three, Step 3.2.

7.2 See Method 7000, Step 7.3, Furnace Technique.

8.0 QUALITY CONTROL

8.1 See Section 8.0 of Method 7000.

9.0 METHOD PERFORMANCE

9.1 Precision and accuracy data are not available at this time.

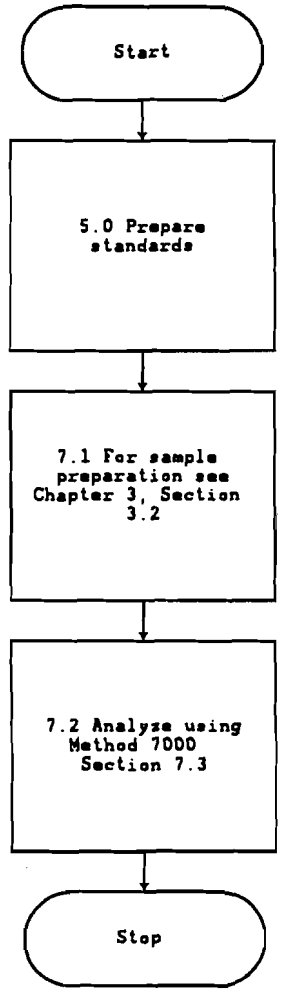
9.2 The performance characteristics for an aqueous sample free of interferences are:

Optimum concentration range: 0.2-4 ug/L.
Detection limit: 0.05 ug/L.

10.0 REFERENCES

1. Methods for Chemical Analysis of Water and Wastes; U.S. Environmental Protection Agency. Office of Research and Development. Environmental Monitoring and Support Laboratory. ORD Publication Offices of Center for Environmental Research Information: Cincinnati, OH, 1983; EPA-600/4-79-020.

METHOD 7951
ZINC (ATOMIC ABSORPTION, FURNACE TECHNIQUE)



APPENDIX

COMPANY REFERENCES

The following listing of frequently-used addresses is provided for the convenience of users of this manual. No endorsement is intended or implied.

Ace Glass Company
1342 N.W. Boulevard
P.O. Box 688
Vineland, NJ 08360
(609) 692-3333

Aldrich Chemical Company
Department T
P.O. Box 355
Milwaukee, WI 53201

Alpha Products
5570 - T W. 70th Place
Chicago, IL 60638
(312) 586-9810

Barneby and Cheney Company
E. 8th Avenue and N. Cassidy Street
P.O. Box 2526
Columbus, OH 43219
(614) 258-9501

Bio - Rad Laboratories
2200 Wright Avenue
Richmond, CA 94804
(415) 234-4130

Burdick & Jackson Lab Inc.
1953 S. Harvey Street
Muskegon, MO 49442

Calgon Corporation
P.O. Box 717
Pittsburgh, PA 15230
(412) 777-8000

Conostan Division
Conoco Speciality Products, Inc.
P.O. Box 1267
Ponca City, OK 74601
(405) 767-3456

Corning Glass Works
Houghton Park
Corning, NY 14830
(315) 974-9000

Dohrmann, Division of Xertex Corporation
3240 - T Scott Boulevard
Santa Clara, CA 95050
(408) 727-6000
(800) 538-7708

E. M. Laboratories, Inc.
500 Executive Boulevard
Elmsford, NY 10523

Fisher Scientific Co.
203 Fisher Building
Pittsburgh, PA 15219
(412) 562-8300

General Electric Corporation
3135 Easton Turnpike
Fairfield, CT 06431
(203) 373-2211

Graham Manufactory Co., Inc.
20 Florence Avenue
Batavia, NY 14020
(716) 343-2216

Hamilton Industries
1316 18th Street
Two Rivers, WI 54241
(414) 793-1121

ICN Life Sciences Group
3300 Hyland Avenue
Costa Mesa, CA 92626

Johns - Manville Corporation
P.O. Box 5108
Denver, CO 80217

Kontes Glass Company
8000 Spruce Street
Vineland, NJ 08360

Millipore Corporation
80 Ashby Road
Bedford, MA 01730
(617) 275-9200
(800) 225-1380

National Bureau of Standards
U.S. Department of Commerce
Washington, DC 20234
(202) 921-1000

Pierce Chemical Company
Box 117
Rockford, IL 61105
(815) 968-0747

Scientific Glass and Instrument, Inc.
7246 - T Wynnwood
P.O. Box 6
Houston, TX 77001
(713) 868-1481

Scientific Products Company
1430 Waukegon Road
McGaw Park, IL 60085
(312) 689-8410

Spex Industries
3880 - T and Park Avenue
Edison, NJ 08820

Waters Associates
34 - T Maple Street
Milford, MA 01757
(617) 478-2000
(800) 252-4752

Whatman Laboratory Products, Inc.
Clifton, NJ 07015
(201) 773-5800

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