# Title 40 CFR Part 191
# Compliance Certification Application
# for the
# Waste Isolation Pilot Plant

## Appendix VCMP

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United States Department of Energy
Waste Isolation Pilot Plant

Carlsbad Area Office
Carlsbad, New Mexico

# Volatile Organic Compound Monitoring Plan

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# 1.0 INTRODUCTION

This document describes the confirmatory monitoring plan for volatile organic compounds (VOC) which may be entrained in the exhaust air from the Waste Isolation Pilot Plant (WIPP), Carlsbad, New Mexico, during the disposal phase at the facility. This Monitoring Plan is designed to confirm the demonstration contained in the No-Migration Variance Petition (NMVP) that there will be no migration of VOCs from WIPP exceeding concentrations that pose unacceptable risks to human health and the environment. This Monitoring Plan includes the monitoring design, a description of sampling and analysis procedures, and quality assurance (QA) objectives and reporting activities.

## 1.1 BACKGROUND

The WIPP project was authorized by the U.S. Congress to provide a research and development facility to demonstrate the safe disposal of radioactive wastes resulting from national defense activities and programs. The WIPP facility is constructed in a massive underground salt bed formation, with its design characterized as a "room and pillar" arrangement, allowing containerized solids or solidified waste to be placed in the excavations. Waste, equipment, and personnel enter the underground facility through designated shafts.

The hazardous waste management units, defined as waste panels, are located 2150 feet (ft)(655 meters(m)) below ground surface, in the WIPP underground. The waste panels consist of seven rooms and two access drifts each. Each room is approximately 300 ft (91 m) long, 33 ft (10 m) wide, and 13 f (4 m) high. Access drifts connect the rooms and have the same cross section. The U.S. Department of Energy (DOE) intends to operate the facility in a manner that minimizes the number of panels that are open at any one time.

The panels provide room for 6.2 million cubic feet ($ft^3$)(175,600 cubic meters ($m^3$)) of transuranic (TRU) waste, of which 250,000 $ft^3$( 7080 $m^3$) may be remote handled (RH) TRU waste. The remainder will be contact handled (CH) TRU waste. The CH TRU waste package assemblies will be stacked up to three containers high across the width of the room in an interlocking triangular pitch. The RH TRU waste canisters will be inserted into predrilled horizontal holes bored into the room wall of the disposal area. The facility performance objectives are derived from 40 Code of Federal Regulations (CFR) Part 268 and are directed at permanently isolating the waste from the biosphere.

The NMVP (DOE, 1996) demonstrates theoretical compliance with the requirements of 40 CFR Part 268.6, which allows the disposal of wastes prohibited from land disposal only if it can be demonstrated that, to a reasonable degree of certainty, there will be no migration of hazardous constituents from the disposal unit for as long as the wastes remain hazardous. This Confirmatory Monitoring Plan describes a sampling and analysis program to confirm the theoretical no-migration calculations contained in the NMVP. The monitoring program will be capable of quantifying VOC concentrations in ambient mine air at WIPP. As demonstrated in the NMVP, other media are not considered viable contaminant transport pathways during the WIPP operational time frame and are therefore not addressed in this program. By the nature of WIPP operations, there is no credible mechanism for direct release of hazardous constituents to water or soil during the operational time frame.

For the disposal phase, the mine ventilation system is the only possible migration pathway.

Accordingly, this Confirmatory Monitoring Plan is designed to confirm that there will be no migration of VOCs from disposed wastes in the WIPP repository via the air pathway during the Disposal Phase. This plan addresses the following information requirements:

1. Rationale for the design of the monitoring program, based on:
   - Possible migration pathways from WIPP during the active life of the facility
   - Operations at WIPP
   - Strength of engineered and natural material components at WIPP
   - Optimum location of the hazardous constituent monitoring stations to confirm the migration calculations contained in the NMVP
2. Descriptions of the specific elements of the monitoring program, including:
   - The type of monitoring conducted
   - The location of the monitoring stations
   - The monitoring interval

- The specific hazardous constituents monitored
- The implementation schedule for the monitoring program
- The equipment used at the monitoring stations
- Sampling and analytical techniques used
- Data recording/reporting procedures

The results of baseline VOC monitoring at WIPP were used, in part, to refine the monitoring program that will be established for the Disposal Phase, during which full-scale waste emplacement activities will occur. The baseline VOC monitoring results are presented in Appendix BAD of the NMVP, and the environmental monitoring currently anticipated during both the operational and post-closure phases are presented in Chapter 6 of the NMVP.

## 1.2 WASTE DISPOSAL

The DOE will operate and maintain WIPP so that it is free of both chemical and radiological contamination. Therefore, as allowed by New Mexico Administrative Code 4.1, Subpart V §264.13, and consistent with joint U.S. Environmental Protection Agency (EPA) and U.S. Nuclear Regulatory Commission guidance, all waste sampling and analyses are conducted by DOE generator sites in accordance with established procedures. The generator conducts the required waste characterization activities for each container of waste to be sent to WIPP under a QA program. The reports resulting from waste characterization activities are then reviewed for completeness and acceptability at WIPP prior to transport of the wastes.

Waste will be disposed of in the seven rooms of a panel. Each panel will be closed when it is full using a panel closure system installed in each of the two panel access drifts as described in Appendix CLP of the NMVP. The closure system conceptual design consists of concrete block bulkheads and a poured concrete bulkhead. The concrete block bulkheads provide a ventilation barrier while the concrete bulkhead is being installed. The concrete component provides strength and stability for maintenance-free service during the operational period. The DOE's analysis of the bulkhead shows that the structure has sufficient rigidity and compressive strength to remain stable for creep and short-term dynamic loadings. Once a panel has been filled and closed, it will be managed per the requirements of the WIPP RCRA Part B Permit and a No-Migration Determination.

## 1.3 OBJECTIVES OF THE VOLATILE ORGANIC COMPOUND CONFIRMATORY MONITORING PLAN

As described in the NMVP, minute quantities of VOCs could be released from open and closed panels located at WIPP during the disposal phase of the project. Chapter 5 of the NMVP contains a demonstration that any VOCs released from panels would be below any concentrations of concern (COC). This plan describes how VOCs released from waste panels will be monitored to confirm the VOC concentration estimates contained in the NMVP. This plan is responsive to requirements of 40 CFR Part 268.6 and addresses confirmatory monitoring of waste management activities during the WIPP disposal phase.

## 2.0 TARGET VOLATILE ORGANIC COMPOUNDS

The wastes proposed for disposal at WIPP are described in Chapter 4 of the NMVP. Approximately 60 percent of the waste proposed to be emplaced at WIPP during the entire lifetime of the facility is classified as TRU mixed waste, which consists of waste that contains both radioactive and Resource Conservation and Recovery Act (RCRA)-regulated hazardous chemical components.

Generator knowledge of the wastes and the processes by which they are generated, as well as available analytical data, indicate that the VOCs most commonly present in the wastes and responsible for approximately 99 percent of the calculated RCRA-constituent posed human health risk (Appendix WAP of the NMVP) are as follows:

- 1,1-Dichloroethylene
- Carbon tetrachloride
- Methylene chloride
- Chloroform
- 1,1,2,2-Tetrachloroethane
- 1,1,1-Trichloroethane
- Chlorobenzene
- 1,2-Dichloroethane

- Toluene

Physical and chemical data for these target VOCs are presented in Table 2.1.

## 2.1 SOURCES OF VOLATILE ORGANIC COMPOUND EMISSIONS

Figure 2.1 depicts the initial WIPP underground facility configuration. Potential waste-related sources of VOCs include: 1) open panels containing vented waste drums, and 2) closed panels of disposed waste. Any VOC emissions from emplaced waste will pass by a monitoring system as it is directed to the exhaust shaft. Other activities not related to normal waste management activities may also lead to VOC emissions.

Nonwaste-related sources of VOCs at WIPP include background sources and emissions from operational activities in ambient mine air. Background sources of VOCs include any sources that emit VOCs to the ambient air that are drawn into the air intake shaft of the underground WIPP facility. Examples of background sources are oil and gas exploration and petroleum production activities in the WIPP vicinity, potash production, and motor vehicle emissions in the WIPP parking lot and on nearby roads. Sources of VOC emissions also exist below ground surface that are related to WIPP mine operational activities. Fuel combustion, painting activities, cleaning solvents, equipment exhaust, and air conditioners are potential sources of VOCs.

Chapter 5 of the NMVP establishes COCs for the VOCs from waste in open and closed panels. Therefore, the VOC Confirmatory Monitoring

Plan is designed to differentiate VOC concentrations attributed to open and closed panels from other potential sources. Accordingly, VOC monitoring performed to confirm the calculations in the NMVP will begin when waste emplacement commences in the first panel. Potential VOC sources other than open and closed panels will not be directly monitored at WIPP.

## 2.2 MIGRATION PATHWAY

The only pathway for migration of VOCs to the unit boundary during the operational phase is via airborne transport. Any VOCs released in the underground facility would become entrained in the underground ventilation air and released to the atmosphere through the exhaust shaft (Figure 2.1).

Chapter 5 of the NMVP identifies COCs in the Drift E-300 air pathway for the target VOCs. COCs at the panels have been extrapolated from the levels of concern at the unit boundary using a mathematical dispersion model and facility ventilation design data.

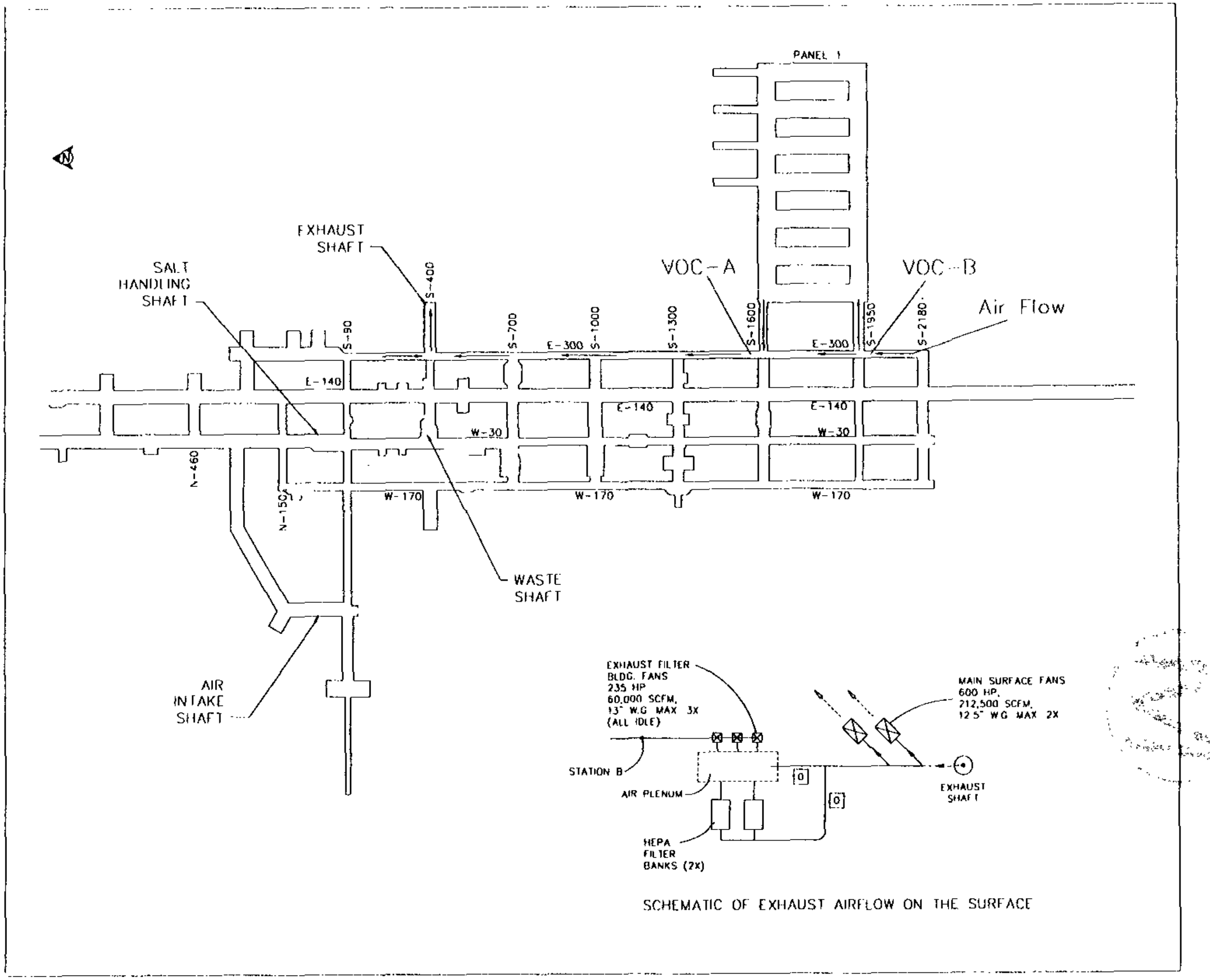

Figure 2.1 Panel Area Air Flow

# 3.0 MONITORING DESIGN

Detailed design features of the VOC Confirmatory Monitoring Plan are presented in this section. The purpose of this program is to confirm that there is no migration of specific target VOCs exceeding any COC. This monitoring plan uses available sampling and analysis techniques to measure VOC concentrations. Available sampling equipment includes the standard WIPP VOC canister samplers with minor modifications.

## 3.1 SAMPLING LOCATIONS

Air samples will be collected at two locations in the facility to quantify airborne VOC concentrations. VOCs emanating from Panel 1 will be measured by placing one VOC monitoring station just downstream from Panel 1 at VOC-A and another station upstream from Panel 1 at VOC-B (Figure 2.1). In this configuration VOC-B will measure VOC releases from the upstream sources (i.e., Panel 2) and other background sources of VOCs, and VOC-A will measure upstream VOC releases plus any additional releases from Panel 1. A sample will be collected from each station on designated sample days. For each quantified target VOC, the concentration measured at VOC-B will be subtracted from the concentration measured at VOC-A to assess any release from Panel 1. Measurements from the first panel will confirm estimates of releases from all panels since the releases will be cyclic from panel-to-panel.

The sampling locations were selected based on operational considerations and the calculations presented in Chapter 5 of the NMVP. As discussed in Section 2.0, there are several different potential sources of release for VOCs. These sources include incoming air from above ground, facility support operations, open waste panels, and closed waste panels. In addition, because of the ventilation requirements of the underground facility and atmospheric dispersion characteristics, any VOCs that are released from Panel 1 may be difficult to detect and differentiate from other sources of VOCs at any underground or above ground location further downstream of Panel 1. By measuring VOC concentrations close to the potential source of release (i.e., Panel 1), it will be possible to differentiate potential releases from background levels and confirm the theoretical calculations included in the NMVP.

### 3.1.1 E-300 Panel 1 Air Outlet (Station VOC-A)

Panel 1 will be the first open panel, and it will become the first closed waste panel once it is filled and the panel closure systems are installed and certified. Waste disposal activities will continue in Panel 2 during closure of Panel 1. Because Panel 1 is a potential source of VOC releases to the ventilation air traveling to the exhaust shaft, sampling station VOC-A has been established in the Drift E-300 downstream of the Panel 1 air outlet (Drift S-1600). The purpose of this station is to evaluate whether the concentrations of VOCs measured at this point are sufficiently higher than upstream concentrations to indicate potential migration from Panel 1. Therefore, concentrations of VOCs measured upstream of Panel 1 will be subtracted from those measured at station VOC-A and the resulting differences will be compared to the calculated COCs for Drift E-300.

The COCs for releases from waste panels have been calculated for each of the target VOCs in the Drift E-300 under normal operational conditions (see Chapter 5 of the NMVP). The calculated COC difference between VOC-A and VOC-B, is presented in Table 3.1 for each of the nine target compounds, in terms of micrograms per cubic meter ($\mu g/m^3$) and parts per billion by volume (ppbv). As presented in Appendix BAD of the NMVP, baseline VOC monitoring has been performed at WIPP for three of the target VOCs (i.e., carbon tetrachloride, methylene chloride, and 1,1,1-trichloroethane). The average measured concentrations of these compounds entrained in the facility exhaust air are less than 2 percent of the COC presented in Table 3.1. These data demonstrate that it will be possible to differentiate between the VOC concentrations measured at VOC-A and VOC-B for comparison to the COCs presented in Table 3.1.

### 3.1.2 E-300 Panel 2 Air Outlet (Station VOC-B)

To quantify VOC concentrations upstream of Panel 1, another sampling station will be established in Drift E-300 downstream of the Panel 2 air outlet. Results from this monitoring station will allow target VOC concentrations in the ventilation air upstream of Panel 1 to be distinguished from any target VOCs that may be released from Panel 1. VOC concentrations measured at this location will consist of background concentrations entering the facility through the Air Intake Shaft, concentrations attributed to upstream facility operations, and concentrations from waste disposal activities in open Panel 2 after Panel 1 is closed. For each sampling event, target compound concentrations detected at VOC-B will be subtracted from those measured at VOC-A to assess VOC releases from Panel 1.

## Table 3.1: Volatile Organic Compound Concentrations of Concern*

| Compound | Molecular Weight (g/mol) | Drift E-300<br>µg/m³ | Drift E-300<br>ppbv |
|---|---|---|---|
| 1,1-Dichloroethylene | 96.95 | 106 | 27 |
| Carbon tetrachloride | 153.8 | 35 | 6 |
| Methylene chloride | 84.94 | 1,130 | 326 |
| Chloroform | 119.4 | 23 | 5 |
| 1,1,2,2-Tetrachloroethane | 167.9 | 92 | 13 |
| 1,1,1-Trichloroethane | 133.42 | 3,300 | 600 |
| Chlorobenzene | 112.6 | 10,000 | 2,300 |
| 1,2,-Dichloroethane | 98.96 | 20 | 10 |
| Toluene | 92.13 | 212,000 | 57,000 |

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| | |
|---|---|
| g/mol | Grams per mole |
| µg/m³ | Micrograms per cubic meter |
| ppbv | Parts per billion by volume |

* Calculated at 25 degrees Celsius (°C) and 760 millimeters of mercury (mmHg).

## 3.2 ANALYTES TO BE MONITORED

Based on acceptable knowledge, previous analytical data, and recent risk calculations (Appendix WAP and Chapter 5 of the NVMP), nine VOCs have been initially identified for monitoring. These compounds are listed in Table 2.1. The analysis will focus on routine detection and quantification of these compounds in collected samples. Other compounds may also be present in the samples. As part of the analytical evaluations, the presence of other compounds will be investigated. The analytical method will allow semi-quantitative evaluation of these compounds as tentatively identified compounds (TIC).

## 3.3 SAMPLING AND ANALYSIS METHODS

A technically sound, reliable, and versatile sampling method is required for the VOC monitoring program. The selected method must be able to definitively identify and quantify the initial nine target compounds. Another consideration is the desire to use EPA approved or recommended methods that provide data of known and documented quality. In addition, the present WIPP program includes a comprehensive VOC monitoring program established at the facility; equipment, training, and documentation for VOC measurements are already in place.

The method selected for VOC sampling is EPA Compendium Method TO-14 (EPA, 1988b; Winberry and others, 1990). The TO-14 sampling technique uses 6-liter SUMMA® passivated stainless-steel canisters to collect integrated air samples at each sample location. This method will be used for guidance in collecting the samples at WIPP. The samples will be analyzed using gas chromatography/mass spectrometry (GC/MS) under an established Quality Assurance/Quality

Control (QA/QC) program (WP 12-7) following guidance from the Draft EPA CLP-SOW for Volatile Organics Analysis of Ambient Air in Canisters (EPA, 1991). The Quality Assurance Project Plan (QAPP), WP 12-7, was prepared for the baseline monitoring program at the WIPP. It will be updated once the confirmatory monitoring plan is finalized.

The TO-14 method is an EPA-recognized sampling procedure for VOC sampling and speciation. It can be used to provide integrated samples, or grab samples, and compound quantitation for a broad range of concentrations. The sampling system can be operated unattended but requires detailed operator training.

As presently designed, the field sampling systems will be operated in the pressurized mode. In this mode, air is drawn through the inlet and sampling system with a pump. The air is pumped into an initially evacuated SUMMA® passivated canister by the sampler, which regulates the rate and duration of sampling. The passivation process forms a pure chrome-nickel oxide on the interior surfaces of the canisters. This type of container has been used routinely at WIPP in the past and has demonstrated sample storage stability for a wide variety of VOCs. At the end of each sampling period, the canisters will be pressurized to about two atmospheres absolute. In the event of shortened sampling periods or other sampling conditions, the final pressure in the canister may be less than two atmospheres absolute. Sampling duration will be approximately six hours, so that a complete sample can be collected during a single work shift.

The canister sampling system and GC/MS analytical method are particularly appropriate for the VOC Confirmatory Monitoring Program because a relatively large sample volume is collected, and multiple dilutions and reanalyses can occur to ensure identification and quantification of target VOCs within the working range of the method. The contract required quantitation limits (CRQL) proposed by EPA are 5 ppbv or less for the nine target compounds (EPA, 1991), so that low concentrations can be measured. CRQLs are the EPA-specified levels of quantitation for EPA contract laboratories that analyze canister samples by GC/MS. The CLP-SOW expressly states how instrument detection limits are demonstrated. For the purpose of this monitoring plan, the CRQLs are defined as the method reporting limits (MRL). The MRL is a function of instrument performance, sample preparation, sample dilution, and all steps involved in the sample analysis process.

Detailed analytical standard operating procedures (SOP) and a QAPP have been prepared for EPA Method TO-14 canister analysis as part of the baseline VOC monitoring at WIPP. Revisions to these documents will be made as necessary to meet the QA/QC objectives described in Section 5.0. In addition, canister and sampling system cleaning and certification SOPs and QAPPs have been prepared. These procedures and plan will be consistent with the QA/QC objectives defined for the program.

Alternative sampling methods will be considered for deployment. One option will be to use subatmospheric samplers rather than pressurized sampling systems for stations VOC-A and VOC-B. In addition, remote sensing by proposed draft EPA Method TO-16, open-path fourier transform infrared spectroscopy (OP-FTIR) and extractive FTIR, may constitute supplemental or alternative methods for detecting VOCs released from waste panels at WIPP. WIPP personnel will continue to follow the development of emerging FTIR technology, and other potentially applicable technologies for assessing VOCs in the WIPP environment. Real-time monitoring with a FTIR system may be a feasible future option for the VOC Confirmatory Monitoring Program.

## 3.4 Sampling Schedule

Many tasks will be completed prior to the initiation of VOC monitoring according to the monitoring plan. For example, power will be run to the monitoring station locations, engineering drawings will be created/revised for the monitoring stations, and program QAPP and SOP documentation will be finalized. Some sampling will be conducted prior to waste emplacement to troubleshoot the monitoring system. The purpose of collecting data during this phase will be to evaluate whether the monitoring systems and analytical methods are properly functioning. The troubleshooting period will be determined by VOC monitoring group personnel.

Confirmatory VOC sampling at Stations VOC-A and VOC-B will begin with initial waste emplacement in Panel 1. Sampling will continue during Panel 1 operations and will end no earlier than 6 months after the certified closure of Panel 1.

The environment within Panel 1 is not expected to vary substantially from day to day. If releases from Panel 1 do occur, concentrations in Drift E-300 may increase gradually over time as the panel is filled. Once the panel is filled and closed, the panel closure systems are designed to minimize air leakage from the relatively static panel environment. For these reasons, routine sampling will be conducted twice a week during the time Panel 1 is filled and for the first 6 months after the closure of Panel 1 has been certified.

VOC concentrations will be evaluated quarterly to assess whether the sampling results represent adequate confirmation of the emission calculations. If the average measured concentrations for the Panel 1 monitoring period confirm the calculations, no additional sampling will be performed. Confirmation will be achieved if the annual average concentration is below the predicted value. Monitoring will be extended for at least 12 months if no emissions are detected. However, the sampling frequency will be decreased to one per week. In addition, if a 12-month average target compound concentration exceeds the concentration of concern, additional sampling will be considered.

# 4.0 SAMPLING AND ANALYSIS PROCEDURES

This section describes the equipment and procedures that will be implemented during sample collection and analysis activities for VOCs at WIPP.

## 4.1 SAMPLING EQUIPMENT

The sampling equipment that will be used during the study includes the following: 6-liter (L) stainless-steel SUMMA® canisters, and VOC canister samplers. A discussion of each of these items is presented below.

### 4.1.1 SUMMA® Canisters

Six-liter, stainless-steel canisters with SUMMA® passivated interior surfaces will be used to collect and store all ambient air and gas samples for VOC analyses collected as part of the monitoring processes. These canisters must be cleaned and certified prior to their use, as described by Compendium Method TO-14 and the draft EPA CLP-SOW for Analysis of Ambient Air in Canisters. A SOP describing this process in detail has been prepared by the analytical laboratory. Compendium Method TO-14 and the CLP-SOW (EPA, 1991) were used as guidance documents in the preparation of this SOP.

### 4.1.2 Volatile Organic Compound Canister Samplers

A conceptual diagram of a VOC sample collection unit is provided in Figure 4.1. Unless an alternate sampling method is selected, two

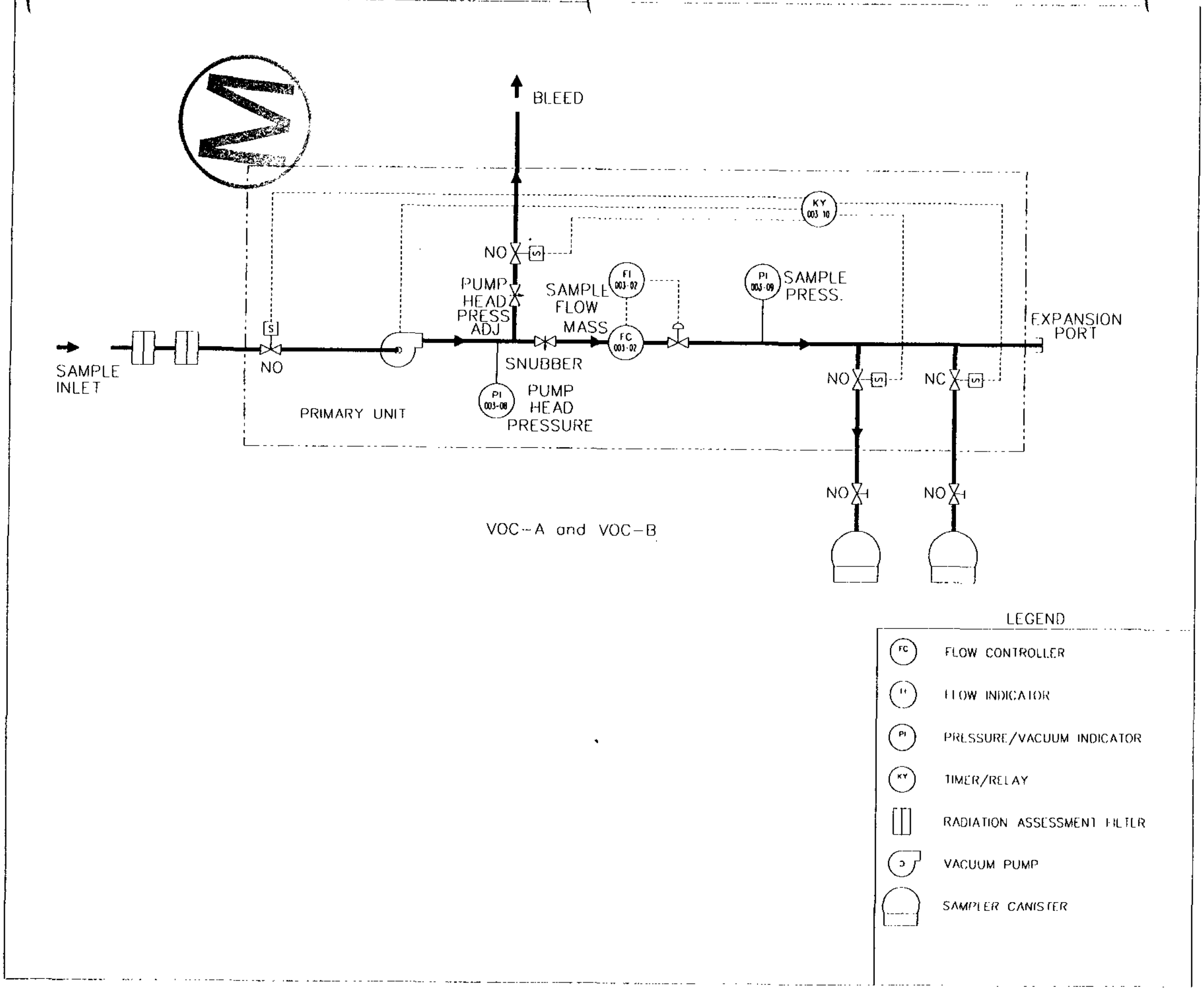

Figure 4.1 – VOC Monitoring System Design

such systems, VOC-A and VOC-B, will be operational at the time waste disposal operations begin in Panel 1. The sampling system consists of a sample pump, flow controller, sample inlet, two inlet filters in series to remove particulate matter, vacuum/pressure gauge, electronic timer, inlet purge vent, two sampling ports, and sufficient collection canisters so that any delays attributed to laboratory turnaround time and canister cleaning and certification will not result in canister shortages. Knowledge of sampler flow rates and duration of sampling will allow calculation of sample volume. The set point flow rate will be verified during sample collection by monitoring the mass flow indication. Prior to use, the sample collection units, including inlet line, will be tested and certified to demonstrate that they are free of contamination above the reporting limits of the VOC analytical method (see Section 5.0). Ultra high purity humidified zero air will be pumped through the sampling unit and collected in previously certified canisters as sampler blanks for analysis, as described in WP 12-7. A SOP describing in detail the cleaning and certification procedure for samplers (including pressure testing and target compound recovery evaluation) has been prepared.

## 4.2 SAMPLE COLLECTION

Samples collected from the underground facility should be representative of routine operations; therefore, six-hour integrated samples will be collected on each sample day. Alternative sampling durations may be defined for experimental purposes. The VOC canister sampler at each location will sample ambient air on the same programmed schedule. The sample pump will be programmed to sample continuously over a six-hour period during the work day. The units will sample at a nominal flow rate of 33.3 actual milliliters per minute over a six-hour sample period.

This schedule will yield a final sample volume of approximately 12 L. Flow rates and sampling duration may be modified as necessary for experimental purposes and to meet the data quality objectives.

Sample flow will be checked each sample day using the in-line mass flow controller. These flow controllers are initially factory-calibrated and specify a typical accuracy of better than 10 percent full scale. Additionally, each air flow controller is calibrated at a manufacturer-specified frequency using a National Institute of Standards and Testing (NIST) primary flow standard. Existing SOPs have been revised to address the specific calibration requirements of the VOC monitoring equipment.

Upon initiation of waste disposal activities in Panel 1, samples will be collected twice each week (at Stations VOC-A and VOC-B). Samples collected at the panel locations should represent the same matrix type (i.e., elevated levels of salt aerosols). To verify the matrix similarity, duplicate samples will be collected from each sampling station (stations VOC-A and VOC-B) during the first sampling event and at an overall frequency of five percent thereafter (see Section 5.1).

## 4.3 SAMPLE MANAGEMENT

Field sampling data sheets will be used to document the conditions under which each sample is collected. These data sheets have been developed specifically for VOC monitoring at the WIPP facility. The individuals assigned to collect the specific samples will be required to fill in all of the appropriate sample data and to maintain this record in sample logbooks. The program team leader will review these forms for each sampling event.

All samples will be maintained, and shipped if necessary, at ambient temperatures. Collected samples will be transported in appropriate containers. Prior to leaving the underground for analysis, all sample containers must undergo radiological screening. No potentially contaminated samples or equipment will be transported to surface.

Additional QA requirements for sample management contained in the sitewide Quality Assurance Program Description, WP 13-1, will be followed as appropriate. Chain-of-custody procedures will be followed closely, and additional requirements imposed by the laboratory for sample analysis will be included as necessary.

Individuals collecting samples will be responsible for the initiation of custody procedures. The chain of custody will include documentation as to the canister certification, location of sampling event, time, date, and individual handling the samples. Samples will be collected and handled in accordance with WP 12-7 and approved SOPs. Deviations from procedure will be considered a variance. Variances must be preapproved by the program manager and recorded in the project files. Unintentional deviations, sampler malfunctions, and other problems are nonconformances. Nonconformances must be documented and recorded in the project files. All field logs/data sheets must be incorporated into WIPP's records management program.

More detailed documentation of sample management is presented in WP 12-7, the QAPP for the VOC Monitoring Program (to be updated as described in Section 3.3).

## 4.4 SAMPLER MAINTENANCE

Routine sampler maintenance will be the responsibility of the sampling personnel. This maintenance will include, but not be limited to, replacement of damaged or malfunctioning parts without compromising the integrity of the sampler, filter changes, leak testing, and minor cleaning. Major cleaning and sampler cleanliness certification will be the responsibility of the sampling and analytical laboratory personnel. Additionally, complete spare units will be maintained onsite to minimize downtime because of sampler malfunction. A sampler preventative maintenance schedule has been developed and is included in WP 12-7. At a minimum, samplers will be certified for cleanliness initially, after any parts that are included in the sample flow path are replaced, or any time analytical results indicate potential contamination. All sample canisters will be certified prior to each usage.

## 4.5 ANALYTICAL PROCEDURES

Analytical procedures used in the analysis of VOC samples from canisters are based on EPA guidance in Compendium Method TO-14 (EPA, 1988b) and in the Draft CLP-SOW for Analysis of Ambient Air (EPA, 1991). Specific analytical SOPs and method validation data are in place at the program analytical laboratory for the performance of canister sample analyses. The technical approach for canister sample analysis is summarized below.

### 4.5.1 Sample Preparation

Because canisters will be pressurized during the sampling procedure, laboratory pressurization will not be necessary for analyses. Canister pressures will be verified by the laboratory when they are received to confirm that significant losses did not take place during shipping and storage.

### 4.5.2 Analytical System Requirements

The GC/MS analytical system will consist of three major components: the sample introduction system, analyte separation system (GC), and the analyte detector system (MS).

- Sample Introduction System for Canisters: This system will include a drying tube to remove moisture from the gas stream. One or more cryogenic traps may be used to focus and desorb trapped material. Transfer lines within the introduction unit will be heated as necessary so that volatile compounds are not actively absorbed. Valves and solenoids will be heated and be of a low dead volume type. The introduction system will have an in-line mass flow controller. The introduction unit will be capable of introducing internal standards directly into the sample flow path.

- Analyte Separation: Analyte separation will be achieved by GC. The GC will be capable of subambient temperature programming.

- Detection System: Analyte detection will be accomplished by MS. The MS must be capable of scanning from 35 to 300 mass to charge ratio in one second or less, be fitted with a gas jet separator, a data system capable of storing all raw data, and a computer algorithm for analyte quantitation and forward library searching. All raw and processed GC/MS data must be stored on magnetic tape or disk and kept for the duration of this project.

### 4.5.3 Standard Preparation

Primary analytical standards will be prepared by the laboratory from commercially available, certified calibration gases. Alternatively, primary standards may be generated internally by the laboratory. Primary standards of analytes that are gases at standard temperature and pressure (STP) may be internally prepared in a static gas dilution bottle. For analytes that are liquid or solid at STP, a mixture may be made and loaded directly into a standard preparation cylinder. These internally generated standards will be checked against EPA audit cylinders or other reference materials to verify the accuracy of their concentrations.

Primary standards will be prepared for the nine target compounds as well as the internal standards. Secondary standards used for instrument calibration will be prepared from dilution of the primary standards.

### 4.5.4 Calibration Procedures

Prior to the analysis of a standard curve, the GC/MS system must undergo a mass calibration check. This check is performed by injecting 50 nanograms (ng) of 4-bromofluorobenzene (BFB) directly onto the capillary column. The requirements (criteria) for relative ion abundances for BFB, listed in Table 4.1, must be met before analyses may proceed. BFB requirements must be met for each 12 hours of operation.

Quantitative standards for the nine target analytes will be analyzed at five concentrations. These concentrations should define the linear range of the instrument for these nine compounds; however, if some nonlinearity exists, concentrations may be determined by curve fitting or physically plotting the data. One standard concentration shall be at or near a concentration corresponding to the required MRL for each target compound. Relative response factors will be generated for each target compound. These response factors must meet the requirements listed in Section 5.1.3. As discussed above, if low concentration standards do not meet the linearity requirement, then a curve-fitting routine may be used. The method used to quantify the data must be reported with the analytical results.

Table 4.1 goes here

### 4.5.5 Library Searches

In every sample analyzed, a forward search of the NIST library of mass spectra must be performed for all chromatographic peaks greater than 10 percent of the nearest internal standard.

### 4.5.6 Data Reporting

Sample target analyte concentrations will be quantified using the mid-range calibration standards and will be reported in ppbv. Non-target sample contaminants identified by NIST library searches will be reported as TICs, and concentration calculations will be based on the response of the nearest internal standard. The relative response factor used for quantitation, as well as copies of spectra with the library search results (purity and fit), will be submitted with the results. A table listing the run sequence with the corresponding internal standard area counts must be reported with the analytical results. A narrative describing any problems with sample analysis must be included. Any nonconformances must be included with the reporting of the data. Data reporting and documentation requirements are discussed in greater detail in WP 12-7.

## 4.6 LABORATORY SELECTION

Sample analyses will occur at the WIPP onsite analytical laboratory and/or at a suitable contract analytical laboratory. Upon selection of an offsite contract laboratory, measures shall be taken, in accordance with the current Westinghouse Waste Isolation Division procurement policies and procedures, to ensure that procured services conform to specified requirements. These measures will generally include one or more of the following: 1) evaluation of the supplier's capability to provide services in accordance with requirements, including a history of providing similar services; 2) evaluation of objective evidence of conformance, such as laboratory document submittals; and 3) examination of delivered services.

## 4.7 LABORATORY PROCEDURES

Analytical laboratories that perform analyses for the VOC Confirmatory Monitoring Plan are required to develop and maintain, at a minimum, the following SOPs:

- Canister cleaning and certification
- Sampler cleaning and certification
- Analysis of VOCs in SUMMA® canisters
- Data QA and reporting

Laboratories are also required to maintain an internal program QA Manual, and to develop and prepare a QAPP covering cleaning and certification of canisters and laboratory analysis of canister samples. In addition, laboratories will be required to review and comply with WP 12-7.

# 5.0 QUALITY ASSURANCE

Many quality assurance objectives for the VOC Confirmatory Monitoring Plan have been addressed in Sections 3.0 and 4.0. For example, sample collection procedures are discussed, including justification of sampling location selection. Additional topics include discussions of sampling program operations, preparation of sampling equipment and sample containers, redundancy in sampling equipment and sample containers (including canister certification), a general sample management/control scheme, and the selection of analytical procedures. More detailed descriptions of these functions, as well as additional quality-related objectives, are addressed in WP 12-7. WP 12-7 has been prepared in accordance with the document entitled "EPA Requirements for Quality Assurance Project Plans for Environmental Data Operations" (EPA, 1994) and the "Interim Guidelines and Specifications for Preparing Quality Assurance Project Plans" (EPA, 1983), and QA criteria listed in Table 5.1. This section addresses the methods to be used to evaluate the components of the measurement system and how this evaluation will be used to assess data quality. In addition, project activities will be performed in conformance with QA requirements described in WP 12-7.

## 5.1 QUALITY ASSURANCE OBJECTIVES FOR THE MEASUREMENT OF PRECISION, ACCURACY, SENSITIVITY, AND COMPLETENESS

Quality assurance objectives for the VOC Confirmatory Monitoring Plan will be defined in terms of the following data quality parameters:

Table 5.1 goes here.

- **Precision.** For the duration of this project, precision will be defined and evaluated by the relative percent difference (RPD) values calculated between field duplicate samples and between laboratory duplicate samples.

$$RPD = \frac{(A - B)}{[(A + B)/2]} \times 100 \tag{3}$$

where:

A = Original sample result

B = Duplicate sample result

- **Accuracy.** Analytical accuracy will be defined and evaluated through the use of analytical standards. Because recovery standards cannot reliably be added to the sampling stream, overall system accuracy must be based on analytical instrument performance evaluation criteria. These criteria will include performance verification for instrument calibrations, laboratory control samples, and sample internal standard areas. These criteria will constitute the verification of accuracy for target analyte quantitation (i.e., quantitative accuracy). Evaluation of standard ion abundance criteria for BFB will be used to evaluate the accuracy of the analytical system in the identification of targeted analytes, as well as the evaluation of unknown contaminants (i.e., qualitative accuracy).

- **Sensitivity.** Sensitivity will be defined by the required MRLs for the program. Attainment of required MRLs will be verified by the performance of statistical method detection limit (MDL) studies in accordance with 40 CFR Part 136. The MDL represents the minimum concentration that can be measured and reported with 99 percent confidence that the analyte concentration is greater than zero. An MDL study will be performed by the program analytical laboratory prior to sampling and analysis.

- **Completeness.** Completeness will be defined as the percentage of the ratio of the number of valid sample results received versus the total number of samples collected. Completeness may be affected, for example, by sample loss or destruction during shipping, by laboratory sample handling errors, or by rejection of analytical data during data validation.

### 5.1.1 Evaluation of Laboratory Precision

Laboratory sample duplicates and blank spike/blank spike duplicates (BS/BSD) will be used to evaluate laboratory precision. Quality assuarance objectives for laboratory precision are listed in Table 5.1, and are based on precision criteria proposed by EPA for canister sampling programs (EPA, 1991). These values will be appropriate for the evaluation of samples with little or no matrix effects. Because of the potentially high level of salt-type aerosols in the WIPP underground environment, the analytical precision achieved for WIPP samples may vary with respect to the

EPA criteria. RPDs for BS/BSD analyses will be tracked through the use of control charts. RPDs obtained for laboratory sample duplicates will be compared to those obtained for BS/BSDs to ascertain any sample matrix effects on analytical precision. BS/BSDs and laboratory sample duplicates will be analyzed at a frequency of 10 percent or one per analytical lot, whichever is more frequent. Precision windows and outlier criteria are addressed in WP 12-7.

### 5.1.2 Evaluation of Field Precision

Field duplicate samples will be collected at a frequency of five percent for both monitoring locations. Like the laboratory duplicate data, field duplicate data will be compared to the EPA precision criteria presented in Table 5.1, and matrix and sampling effects on precision will be assessed through comparison with internal laboratory precision data.

### 5.1.3 Evaluation of Laboratory Accuracy

#### Quantitative Accuracy

Quantitative analytical accuracy will be evaluated through performance criteria on the basis of: 1) relative response factors generated during instrument calibration, 2) analysis of laboratory control samples (LCS), and 3) recovery of internal standard compounds. The criteria for the initial calibration (5-point calibration) is that any single relative response factor for a particular target compound can differ by no more than 30 percent from the average of the five. After the successful completion of the 5-point calibration, it is sufficient to analyze only a midpoint standard for every 12 hours of operation. The midpoint standard must pass the 30 percent difference acceptance criteria before sample analysis may begin.

A blank spike or LCS is an internal QC sample generated by the analytical laboratory by spiking a standard air matrix (humid zero air) with a known amount of a certified reference gas. The reference gas will contain the target VOCs at known concentrations. Percent recoveries for the target VOCs will be calculated for each LCS relative to the reference concentrations. Objectives for percent recovery are listed in Table 5.1, and are based on accuracy criteria proposed by EPA for canister sampling programs (EPA, 1991). LCSs will be analyzed at a frequency of 10 percent or one per analytical lot, whichever is more frequent. Recovery windows and outlier criteria are addressed in WP 12-7.

Internal standards will be introduced into each sample analyzed, and will be monitored as a verification of stable instrument performance. In the absence of any unusual interferences, areas should not change by more than 40 percent over a 12-hour period. Deviations larger than 40 percent are an indication of a potential instrument malfunction. If an internal standard area in a given sample changes by more than 40 percent, the sample must be reanalyzed. If the 40 percent criterion is not achieved during the reanalysis, the instrument must undergo a performance check and the midpoint standard must be reanalyzed to verify proper operation. Response and recovery of internal standards will also be compared between samples, LCSs, and calibration standards to identify any matrix effects on analytical accuracy.

#### Qualitative Accuracy

Qualitative accuracy in the identification of target VOCs will be evaluated by the relative ion abundance criteria established for the internal standard compound BFB. For each 12 hours of sample analysis, a 50-nanogram (ng) injection of BFB must be made, and the requirements listed in Table 4.1 must be met before the instrument may be used to analyze samples.

### 5.1.4 Evaluation of Sensitivity

The presence of aerosol salts in underground locations may affect the MDL of the samples collected in those areas. The intake manifold of the sampling systems will be sufficiently protected from the underground environment to minimize salt aerosol interference.

The MDL for each of the nine target compounds will be evaluated by the analytical laboratories before sampling begins. The initial MDL evaluation will be performed in accordance with 40 CFR Part 136 and with EPA/530-SW-90-021, as revised and retitled, "Quality Assurance and Quality Control" (Chapter 1 of SW-846) (1986).

### 5.1.5 Completeness

The expected completeness for this project is greater than or equal to 90 percent. Data completeness will be tracked monthly.

## 5.2 SAMPLE HANDLING AND CUSTODY PROCEDURES

Sample packaging, shipping, and custody procedures are addressed in WP 12-7 (see Sections 7.4 and 8.0).

## 5.3 CALIBRATION PROCEDURES AND FREQUENCY

Calibration procedures and frequencies for analytical instrumentation are listed in Section 4.5.4.

## 5.4 ANALYTICAL PROCEDURES

The analytical procedures for the VOC Confirmatory Monitoring Program, which are based on the draft CLP SOW for Analysis of Ambient Air in Canisters (EPA, 1991) and EPA guidance Method TO-14 (EPA, 1988b), are outlined in Section 4.5.

## 5.5 DATA REDUCTION, VALIDATION, AND REPORTING

Data reduction and validation are addressed in the WP 12-7. A brief description of data reporting is given in Section 4.5; more detail on data reporting is provided in WP 12-7.

A dedicated logbook will be maintained by the operators. This log will contain documentation of all pertinent data for the sampling. Sample collection conditions, maintenance, and calibration activities will be included in this log. Additional data collected by other groups at WIPP, such as ventilation airflow, temperature, pressure, etc., will also be obtained to document the sampling conditions, as necessary.

Data validation procedures will be specified in the monitoring program QA protocols. At a minimum, all field data forms and sampling logbooks will be checked for completeness and correctness. Sample custody and analysis records will be routinely reviewed by the QA officer and the laboratory supervisor.

Data will be summarized quarterly. Data summaries will include target VOC results for each sample collected as well as overall statistical summaries. Graphical summaries may also be included.

## 5.6 PERFORMANCE AND SYSTEM AUDITS

System audits will initially address startup functions for each phase of the project. These audits will consist of onsite evaluation of materials and equipment, review of canister and sampler certification, review of laboratory qualification and operation, and may, at the request of the QA officer, include an onsite audit of the laboratory facilities. The function of the system audit is to verify that the requirements in this plan and the QAPP, have been met prior to initiating the program. System audits will be performed prior to the initiation of the monitoring program.

Performance audits will be accomplished as necessary through the evaluation of analytical quality control data, by performing periodic site audits throughout the duration of the project, and through the introduction of third-party audit cylinders (laboratory blinds) into the analytical sampling stream. Performance audits will also include a surveillance/review of all data associated with canister and sampler certification, a project-specific technical audit of field operations, and a laboratory performance audit. Field logs, logbooks, and data sheets will be reviewed weekly. Blind-audit canisters will be introduced once during the sampling period. Details concerning scheduling, personnel, and data quality evaluation are addressed in WP 12-7.

## 5.7 PREVENTATIVE MAINTENANCE

A brief description of sampler maintenance is described in Section 4.4. Maintenance of analytical equipment will be addressed in the analytical SOP.

## 5.8 CORRECTIVE ACTIONS

Nonconformances and corrective actions of noncomformances will be processed as outlined in the Quality Assurance Program Description (DOE 1994).

## 5.9 QUALITY ASSURANCE REPORTS TO MANAGEMENT

The results of audits will be reported in accordance with sitewide Quality Assurance Plan (QAP) and WP 13-005. Audit reports will include identification of findings and/or observations, as well as an assessment of the effectiveness of the QAP elements review.

# 6.0 ACRONYMS

| | |
|---|---|
| BFB | 4-Bromofluorobenzene |
| BS/BSD | Blank spike/blank spike duplicate |
| CFR | Code of Federal Regulations |
| CH | Contact handled |
| CLP | Contract Laboratory Program |
| COC | Concentration of concern |
| CRQL | Contract required quantitation limit |
| DOE | U.S. Department of Energy |
| EPA | U.S. Environmental Protection Agency |
| g/mol | Grams per mole |
| GC/MS | Gas chromatography/mass spectroscopy |
| LCS | Laboratory control samples |
| MDL | Method detection limit |
| mmHg | Millimeters of mercury |

| | |
|---|---|
| MDL | Method detection limit |
| MRL | Method reporting limit |
| m/z | Mass to charge ratio |
| ng | Nanogram |
| NIST | National Institute of Standards and Testing |
| NMAC | New Mexico Administrative Code |
| NMVP | No-migration variance petition |
| OP-FTIR | Open-path fourier transform infrared spectroscopy |
| ppbv | Parts per billion by volume |
| QA/QC | Quality assurance/quality control |
| QA | Quality assurance |
| QAPD | Quality Assurance Program Description |
| QAPP | Quality Assurance Project Plan |
| QC | Quality control |
| RCRA | Resource Conservation and Recovery Act |
| RH | Remote handled |

| | |
|---|---|
| RPD | Relative percent difference |
| SOP | Standard operating procedure |
| SOW | Statement of work |
| STP | Standard temperature and pressure |
| TIC | Tentatively identified compound |
| TRU | Transuranic |
| UHP | Ultra high purity |
| VOCs | Volatile organic compounds |
| WAC | Waste acceptance criteria |
| WAP | Waste analysis plan |
| WID | Waste Isolation Division |
| WIPP | Waste Isolation Pilot Plant |
| $\mu g/m^3$ | Micrograms per cubic meter |
| °C | Degrees Celsius |

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WP 13-005, Internal and Suppliers QA Audits.

WP 02-9, WIPP Final Safety Analysis Report.

WP 12-7, VOC Monitoring Quality Assurance Project Plan.

WP 13-QA3003, Corrective Action Program.

WP 13-1, WIPP Sitewide Quality Assurance Program.

**Table 2.1: Target Analytes for VOC Monitoring During the WIPP Disposal Phase**

| Target Analyte | Common Synonyms and Acronyms | Chemical Formula | Molecular Weight (g/mol) | Boiling Point (°C)* |
|---|---|---|---|---|
| 1,1-Dichloroethylene | 1,1-Dichloroethene, Vinylidene chloride, 1,1-DCE | $C_2H_2Cl_2$ | 96.95 | 31 |
| Carbon tetrachloride | Tetrachloromethane | $CCl_4$ | 153.8 | 77 |
| Methylene chloride | Dichloromethane | $CH_2Cl_2$ | 84.94 | 40 |
| Chloroform | Trichloromethane | $CHCl_3$ | 119.4 | 61 |
| 1,1,2,2-Tetrachloroethane | sym-Tetrachloroethane, Tetrachloroethane | $C_2H_2Cl_4$ | 167.9 | 147 |
| 1,1,1-Trichloroethane | 1,1,1-TCA, TCA, Methyl chloroform | $C_2H_3CCl_3$ | 133.42 | 74 |
| Chlorobenzene | Monochlorobenzene, Benzene chloride | $C_6H_5Cl$ | 112.6 | 132 |
| 1,2-Dichloroethane | 1,2-DCA, DCA, Ethylene dichloride, EDC, sym-Dichloroethane | $C_2H_4Cl_2$ | 98.96 | 83 |
| Toluene | Methyl benzene | $C_7H_8$ | 92.13 | 111 |

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| | |
|---|---|
| °C | Degrees Celsius |
| VOC | Volatile organic compound |
| WIPP | Waste Isolation Pilot Plant |

* Handbook of Chemistry and Physics, 62nd Edition, CRC Press, 1982.

**Table 3.1: Volatile Organic Compound Concentrations of Concern***

| Compound | Molecular Weight (g/mol) | Drift E-300 | |
|---|---|---|---|
| | | $\mu g/m^3$ | ppbv |
| 1,1-Dichloroethylene | 96.95 | 106 | 27 |
| Carbon tetrachloride | 153.8 | 35 | 6 |
| Methylene chloride | 84.94 | 1,130 | 326 |
| Chloroform | 119.4 | 23 | 5 |
| 1,1,2,2-Tetrachloroethane | 167.9 | 92 | 13 |
| 1,1,1-Trichloroethane | 133.42 | 3,300 | 600 |
| Chlorobenzene | 112.6 | 10,000 | 2,300 |
| 1,2,-Dichloroethane | 98.96 | 20 | 10 |
| Toluene | 92.13 | 212,000 | 57,000 |

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| | |
|---|---|
| g/mol | Grams per mole |
| $\mu g/m^3$ | Micrograms per cubic meter |
| ppbv | Parts per billion by volume |

* Calculated at 25 degrees Celsius (°C) and 760 millimeters of mercury (mmHg).

**Table 4.1: 4-Bromofluorobenzene Key Ions and Ion Abundance Criteria**

| Mass | Ion Abundance Criteria |
|---|---|
| 50 | 8 to 40 percent of mass 95 |
| 75 | 30 to 60 percent of mass 95 |
| 95 | Base Peak, 100 percent Relative Abundance |
| 96 | 5 to 9 percent of mass 95 |
| 173 | <2 percent of mass 174 |
| 174 | >50 percent of mass 95 |
| 175 | 4 to 9 percent of mass 174 |
| 176 | >93 percent but <101 percent of mass 174 |
| 177 | 5 to 9 percent of mass 176 |

**Table 5.1: Quality Assurance Objectives for Accuracy, Precision, Sensitivity, and Completeness**

| Compound | Accuracy (Percent Recovery) | Precision (RPD) | Required MRL (ppbv) | Completeness (Percent) |
|---|---|---|---|---|
| 1,1-Dichloroethylene | 60 to 140 | 25 | 5 | ≥90 |
| Carbon tetrachloride | 60 to 140 | 25 | 2 | ≥90 |
| Methylene chloride | 60 to 140 | 25 | 5 | ≥90 |
| Chloroform | 60 to 140 | 25 | 2 | ≥90 |
| 1,1,2,2-Tetrachloroethane | 60 to 140 | 25 | 2 | ≥90 |
| 1,1,1-Trichloroethane | 60 to 140 | 25 | 5 | ≥90 |
| Chlorobenzene | 60 to 140 | 25 | 2 | ≥90 |
| 1,2-Dichloroethane | 60 to 140 | 25 | 2 | ≥90 |
| Toluene | 60 to 140 | 25 | 5 | ≥90 |

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These data quality objectives are based on control criteria proposed by EPA as presented in the Contract Laboratory Program Statement of Work for the Analysis of Ambient Air in Canisters (EPA, 1991).

| | |
|---|---|
| EPA | U.S. Environmental Protection Agency |
| MRL | Method reporting limit |
| ppbv | Parts per billion by volume |
| RPD | Relative percent difference |