

## CHAPTER 8

### Analysis of Volatile Organic Compounds

#### INTRODUCTION

The WIPP Hazardous Waste Facility Permit, Attachment N, issued by the New Mexico Environment Department under the Resource Conservation and Recovery Act (RCRA), mandates the monitoring of nine volatile organic compounds (VOCs) in the ambient air in the WIPP underground to assure that their respective concentrations of concern are not exceeded. These nine compounds are listed in Table 8-1. Monitoring is conducted in accordance with the “*Confirmatory Volatile Organic Compound Monitoring Plan*”, prepared by the WIPP management and operations contractor, Washington TRU Solutions (WTS). Ambient air samples are collected in six liter Summa or equivalent canisters by Washington Regulatory and Environmental Services (WRES) personnel and delivered for analysis to CEMRC in weekly batches.

CEMRC first began analysis of samples for the Confirmatory VOCs Monitoring Plan in April 2004, using analysts from the Environmental Chemistry (EC) Group and following a successful VOCs program audit by the WTS QA group. At that time, CEMRC had one 6890/5973 Hewlett Packard (now Agilent) gas chromatograph/ mass spectrometer (GC/MS) which had previously been used by Los Alamos National Laboratory (LANL). CEMRC purchased an Entech 7100 Preconcentrator for use as the sample concentration and introduction system. In addition, CEMRC purchased an Entech 3100 Canister Cleaning System for

cleaning and evacuation of canisters after analysis.

#### VOCs PROJECT EXPANSION

The original VOCs laboratory was set up in a small room (149) in the science laboratory wing at CEMRC and only included the equipment necessary for Confirmatory VOCs analysis. In late 2003, the Department of Energy (DOE) requested that CEMRC expand its capabilities to prepare for the analysis of headspace gas (HSG) samples collected from waste drums required under the WIPP Permit, Attachment B. In preparation for this expansion of scope, CEMRC visited the HSG group at LANL to determine the equipment required for the process. Thereafter, a turnkey HSG analysis system consisting of a 6890/5973N Agilent GC/MS with a loop injection system and three Entech 7032 Autosamplers installed in series was purchased from Entech Instruments, Inc. Also included in this purchase was an Entech 3100A oven-based canister cleaning system, an Entech 4600 Dynamic Diluter for automatic preparation of VOCs calibration standards, and fifty 400 mL Silonite-coated mini-canisters with Nupro valves and attached pressure gauges.

After a few months of VOCs Confirmatory Analyses, it became critical to expand the laboratory to accommodate the addition of a backup analysis system. This shortcoming was noted by auditors for the next two years. CEMRC did purchase a backup Preconcentrator to minimize system downtime. However, there was no available space in which to

set up the backup GC/MS instrument even if it were purchased.

With the addition of headspace gas analysis, it was decided in July 2005 to move the VOCs Confirmatory Analysis and Headspace Gas Analysis programs from the EC group into the newly created Organic Chemistry (OC) Group. The primary management focus for the EC group was research oriented, whereas the functions of the OC group were regulatory in nature and required different QA/QC measures and documentation.

Analyses were originally conducted by manually changing the sample attached to the preconcentrator for each sample. Due to the need to maximize efficiency, an Entech 7016 canister autosampler was obtained in June 2005. This autosampler allows for up to sixteen samples to be run in sequence with minimal operator supervision.

Funding was obtained in mid-2005 through a DOE baseline change request to remodel the current CEMRC garage into a functional GC/MS Laboratory. The design for the remodel was completed in late 2005, and construction began in January 2006. Construction was completed in April 2006, and the OC Group moved into the new laboratory.

Around this time, a backup Agilent 6890/5973 GC/MS system was transferred to CEMRC by the Central Characterization Project (CCP) for use in headspace gas analysis. A backup autosampler for HSG analysis was also purchased by CEMRC. Shortly thereafter a new Agilent 6890/5975 GC/MS was obtained with a portion of the lab setup funding to be used as a backup analysis system for the Confirmatory VOCs Monitoring.

The VOCs Confirmatory Monitoring expanded from 353 samples in 2005 to 430 samples in 2006. Increases in sample load are expected in the coming months due to anticipated changes in closed room sampling requirements.

## **METHODS FOR CONFIRMATORY VOCs MONITORING**

Confirmatory VOCs Monitoring requires method detection limits in the lower parts per billion volume (ppbv) range. This type of analysis requires preconcentration of a given volume of ambient air into a much smaller volume prior to introduction into the GC column. In order to maintain performance of the mass analyzer, most of the water vapor and carbon dioxide present in the air sample must be removed prior to analysis. The Entech 7100 Preconcentrator performs these tasks automatically by flowing the sample through three consecutive cryogenic traps at different controlled temperatures. This results in very low detection limits not obtainable without cryogenic preconcentration.

Stock cylinders of Calibration Standard and Laboratory Control Sample gases are purchased certified from a reputable supplier, and then diluted to working concentrations with Ultra-High Purity (UHP) Nitrogen using the Entech 4600 Dynamic Diluter. Canisters are cleaned after sample analysis using the Entech 3100 Canister Cleaning system, which consists of a computerized control module with vacuum pumps and an oven containing a passivated manifold with fittings for connection of canisters. The control software initiates the cleaning of canisters by heating coupled with multiple pressurization/evacuation cycles. A blank sample is analyzed from each cleaning batch as a control to assure proper cleaning has been achieved.

Analysis of VOCs for Confirmatory Monitoring were conducted under procedures using concepts of EPA Air Analysis Compendium Method TO-14A, "*Sampling and Analysis of Ambient Air*". Special quality assurance requirements for these activities were detailed in the "*Quality Assurance Project Plan for Confirmatory Volatile Organic Compound Monitoring*", prepared by WTS. CEMRC personnel wrote procedures for this project under the CEMRC Quality Assurance Plan, which were verified, validated, and placed in the CEMRC Document Control Program. Procedures were composed to include QA requirements from EPA Method TO-14A and all WIPP documents relevant to the Confirmatory Monitoring Program. See Table 8-2 for a list of CEMRC Procedures for Confirmatory Monitoring.

In November, 2006, the WIPP Permit was modified to refer to EPA Air Analysis Compendium Method TO-15, "*Determination of Volatile Organic Compounds (VOCs) In Air Collected In Specially-Prepared Canisters And Analyzed By Gas Chromatography/Mass Spectrometry (GC/MS)*". This method is the most current, having replaced Method TO-14A. It also allows for analysis of a more extensive compound list, in the event that more compounds of interest are added to the list in the future. The CEMRC procedures were modified to account for this change in method.

The permit modification also incorporated an expansion of sampling in the Confirmatory Monitoring Program. Originally, the samples were collected from only two stations in the WIPP underground (VOC-A and VOC-B). The permit change requires sampling from closed rooms within the current panel until the entire panel is full. Therefore, Attachment N now refers to both

Repository VOCs Monitoring and Disposal Room Monitoring. The required detection limits for different types of samples are summarized in Table 8-1.

## **METHODS FOR HEADSPACE GAS ANALYSIS**

The analysis of Headspace Gas (HSG) from waste containers has been conducted at various generator sites prior to shipment of waste to WIPP. In response to request from DOE, CEMRC set up a process for HSG analysis based on the process in use at LANL. Per the WIPP Permit, Attachments B, HSG analysis is conducted using the concepts of EPA Method 8260. Since Method 8260 is a method intended for use with waste matrices, some adaptation was required for HSG analysis. Under the analysis scheme used at CEMRC, HSG samples would be collected into clean, evacuated canisters (SUMMA or equivalent) and shipped to CEMRC for analysis. Upon arrival, sample canisters would be pressurized to twice atmospheric pressure by the addition of an internal standard gas mixture, and then simultaneously analyzed for hydrogen and methane by GC/Thermal Conductivity Detector (TCD) and VOCs by GCMS. The sampling system incorporates three autosamplers in series to allow for the analysis of two complete batches of 20 samples each, plus the requisite QC samples. Samples from the autosamplers pass through heated transfer lines into two injection loops attached to an automated valve for injection into the GC.

The process was preparing to come online in 2004, when CEMRC was informed that this analysis was no longer required. In 2005, CEMRC was again requested to bring the process online, this time under the control of the Central Characterization Program (CCP). CCP required CEMRC

personnel working on HSG activities to do so under their QA process. This required that OC lab personnel be trained to the CEMRC QA process for VOCs Confirmatory Monitoring and the CCP QA process for HSG analysis.

CEMRC HSG procedures were removed from the CEMRC controlled documents program, rewritten to reflect CCP requirements and formats, and placed under the CCP controlled documents program. The CEMRC procurement process was audited by WTS QA to determine whether it met CCP criteria and items which did not were changed. Two CEMRC analysts completed training as HSG analysts in accordance with CCP qualification requirements. A third analyst began his training as well. CEMRC-owned canisters were sent for gauge calibration and helium leak testing in order to qualify for CCP sampling activities.

CEMRC had two backup GCMS systems modified to conform with the CEMRC analysis instrument configuration and purchased an additional autosampler in order to set up a HSG backup analysis system. CEMRC personnel attended weekly meetings with CCP personnel in order to facilitate bringing the HSG project online. New VOCs standards were purchased from a CCP-approved vendor.

## **RESULTS AND DISCUSSION**

### **Confirmatory VOCs Monitoring Program**

A set of 120 preliminary closed/open room samples were analyzed along with VOC-A and VOC-B samples from April 2004 through September 2005. Official closed room sample submission began in August 2006.

Sets of blank and recovery gas samples collected by Shaw Environmental as part

of the sampler cleaning and certification were analyzed in two-day turnaround batches at various times throughout the years, in addition to the regular monitoring samples submitted.

Batch reports are submitted in hardcopy in the EPA Contract Laboratory Program format. An electronic report in the client's specified format is also provided for each batch. Copies of batch reports and all QA records associated with these analyses are maintained according to the CEMRC records management policies, detailed in the QAP.

### **Headspace Gas Analysis**

A preliminary surveillance of the CEMRC Headspace Gas (HSG) Analysis process was conducted by WTS QA in January 2007. Some minor issues were identified and addressed in preparation for the official DOE audit. The DOE audit was conducted in February 2007 by CTAC. CEMRC's HSG analysis process passed the audit and was to be certified to begin HSG sample analysis following successful completion of the Performance Demonstration Program (PDP) cycle in April. PDP samples were received in April 2007 and successfully analyzed. CEMRC was requested by DOE to provide a budget proposal to place the HSG analysis program in cold standby in May 2007.

### **Future Plans for Expansion for VOCs Monitoring in Air**

At the request of WTS, CEMRC analysts investigated the possibility of modifying the method parameters for the HSG GCMS system to allow for screening of high level VOCs in closed room samples and analysis of low level % concentrations of hydrogen and methane. This modification requires no change of the physical configuration of the system. At some future time, the VOCs Confirmatory

Monitoring Program may add hydrogen and methane analysis to the Statement of Work. Cost estimate have been provided to WTS for this potential work.

**Summary Statements**

The success of the Confirmatory VOCs Monitoring Program and the HSG Program demonstrate CEMRC's ability to set up new programs to successfully perform regulatory monitoring tasks in

accordance with specific QA/QC requirements. At the time both programs were proposed, CEMRC did not have qualified staff with experience in similar programs. Existing staff gained knowledge and skills necessary to perform these tasks appropriately in order to pass strict audit criteria.

CEMRC presently has the capability to analyze over 2,000 VOC and HSG samples per year.

**Table 8-1: Compounds of Interest for WIPP Confirmatory Volatile Organic Compounds Monitoring Program**

<b>Compound</b>	<b>Repository Sample Reporting Limit (ppbv)</b>	<b>Closed Room Sample Reporting Limit (ppbv)</b>
1,1-Dichloroethene	5	500
Carbon tetrachloride	2	500
Methylene chloride	5	500
Chloroform	2	500
1,1,2,2-Tetrachloroethane	2	500
1,1,1-Trichloroethane	5	500
Chlorobenzene	2	500
1,2-Dichloroethane	2	500
Toluene	5	500

**Table 8-2: CEMRC Procedures for Confirmatory Volatile Organic Compounds Monitoring Program**

<b>Procedure Number</b>	<b>Procedure Title</b>	<b>Rev.</b>
OC-PLAN-001	Quality Assurance Plan for Analysis of Volatile Organic Compounds in Canister Samples	2
OC-PROC-002	Preparation of Canisters for Ambient Air and Headspace Gas Sampling	2
OC-PROC-003	Gas Chromatography-Mass Spectrometry of Volatile Organic Compounds (VOCs) in Ambient Air from Canisters at PPBV Concentration Levels	1
OC-PROC-004	Preparation of Calibration Standards in Specially Prepared Canisters for Analysis by Gas Chromatography/Mass Spectrometry	2
OC-PROC-005	Data Validation and Reporting of Volatile Organic Compounds from Gas Chromatography/Mass Spectrometry Analysis of Ambient Air in Canisters for the WIPP Volatile Organic Compound Monitoring Program	2
OC-PROC-006	Receipt, Control, and Storage of Gas Samples in Passivated Canisters	1