

CHAPTER 5

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. Compounds consistently detected in ambient air samples in the underground may be added to the list of compounds of interest. Trichloroethylene was added to the analyte list beginning with batch 112907_001. The current list of analytes is presented in Table 5-1.

Monitoring is conducted in accordance with the “*Volatile Organic Compound Confirmatory 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. The program was established and successfully audited by the WTS QA group prior to acceptance of actual samples and is audited at yearly since 2004. 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 purchased a 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.

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 old 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 Volatile Organic Compound Monitoring expanded from 353 samples in 2005 to 430 samples in 2006. Analysis of closed room samples for VOCs, hydrogen, and methane began in 2007 as well and continues to the present. In 2007, CEMRC analyzed a total of 749 samples for VOCs and 182 samples for hydrogen and methane.

Although CEMRC performed well on the DOE audit for the headspace gas analysis project, a decision was made not to submit these samples for analysis at CEMRC. However, some equipment obtained for this project is currently being used for analysis of closed room samples for VOCs and percent levels of hydrogen and methane

METHODS FOR VOLATILE ORGANIC COMPOUND 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.

Analyses for Volatile Organic Compound Monitoring were conducted under procedures using concepts of EPA 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)" (1999).

Special quality assurance requirements for these activities were detailed in the "Quality Assurance Project Plan for 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-15 and all WIPP documents relevant to the Confirmatory Monitoring Program. See Table 5-2 for a list of CEMRC Procedures for Confirmatory Monitoring.

In November, 2006, a WIPP permit modification incorporated an expansion of sampling in the Volatile Organic

Compounds 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 5-1.

METHODS FOR HYDROGEN AND METHANE ANALYSIS

The analysis of hydrogen and methane in closed room samples began with batch 082707_001. Under the analysis scheme used at CEMRC, sample canisters would be pressurized to twice atmospheric pressure (if not already received at above atmospheric pressure) by the addition of ultra high purity nitrogen, and then simultaneously analyzed for hydrogen and methane by GC/Thermal Conductivity Detector (TCD) and screened for VOCs by GCMS. The sampling system incorporates three autosamplers in series to allow for the analysis of two complete batches of six 6L samples per run. Samples from the autosamplers pass through heated transfer lines into two injection loops attached to an automated valve for simultaneous injection into the GC. The VOC screening results are used to determine pre-analysis dilutions required for analysis by Method TO-15. The hydrogen and methane analysis results are reported in separate data packages from the VOCs results.

RESULTS AND DISCUSSION

The OC laboratory analyzed 701 routine ambient air samples for VOCs during 2007. Sets of blank and recovery gas samples collected by Shaw Environmental as part of the sampler cleaning and

certification were analyzed in expedited turnaround batches at various times throughout the years, resulting in analysis of 48 additional samples.

Batch reports for VOCs results 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.

Hardcopy and electronic reports for hydrogen and methane analyses are submitted in the formats specified by the client.

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.

Summary Statements

Because of the proprietary nature of the VOC data, none are reported herein.

The success of the VOCs Monitoring Program and the successful HSG Program audit demonstrate CEMRC's ability to initiate 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 hydrogen/methane samples per year.

Table 5-1: Compounds of Interest for WIPP Confirmatory Volatile Organic Compounds Monitoring Program

Compound	Repository Sample Reporting Limit (ppbv)	Closed Room Sample Reporting Limit (ppbv)
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
Trichloroethylene	2	500

Table 5-2: CEMRC Procedures for Confirmatory Volatile Organic Compounds Monitoring Program

Procedure Number	Procedure Title	Rev.
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	3
OC-PROC-003	Gas Chromatography-Mass Spectrometry of Volatile Organic Compounds (VOCs) in Ambient Air from Canisters at PPBV Concentration Levels	2
OC-PROC-004	Preparation of Calibration Standards in Specially Prepared Canisters for Analysis by Gas Chromatography/Mass Spectrometry	3
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 Plan	3
OC-PROC-006	Receipt, Control, and Storage of Gas Samples in Passivated Canisters	2
OC-PROC-009	Analysis of Hydrogen and Methane in Passivated Canisters Using Gas Chromatography with Thermal Conductivity Detection	0