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Evaluation of Three Analytical Techniques Used to Determine High Levels of Volatile Organic Compounds in Type IV Sludge from Rocky Flats Plant

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EVALUATION OF THREE ANALYTICAL TECHNIQUES USED TO DETERMINE HIGH LEVELS OF VOLATILE ORGANIC COMPOUNDS IN TYPE IV SLUDGE FROM ROCKY FLATS PLANT

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EVALUATION OF THREE ANALYTICAL TECHNIQUES USED TO DETERMINE HIGH LEVELS OF VOLATILE ORGANIC COMPOUNDS IN TYPE IV SLUDGE FROM ROCKY FLATS PLANT

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ABSTRACT

Before disposal, radioactive sludge (Type IV) from Rocky Flats Plant (RFP) must be evaluated for volatile organic compound (VOC) content. The Type IV sludge consists of organic solvents, degreasers, cutting oils, and transuranic (TRU) waste mixed with calcium silicate (MicroCel E®) and Oil Dri® to form a grease or paste-like material. For laboratory testing, a simulated Type IV RFP sludge (nonradioactive) was prepared at Argonne National Laboratory-East. This sludge has a composition similar to that expected from field samples. On the basis of historical information, a typical Type IV sludge is expected to contain approximately 1-10 percent of three target VOCs. The objective of this work is to evaluate three proposed methods for the determination of high levels of these three VOCs in Type IV sludge. The three methods are (1) static headspace gas analysis, (2) methanol extraction, and (3) ethylene glycol extraction. All three methods employ gas chromatography/mass spectrometry (GC/MS). They were evaluated regarding general method performance criteria, ease of operation, and amounts of secondary mixed waste generated.

I. INTRODUCTION

More than 30 volatile organic target analytes are listed in the TRU Waste Characterization Quality Assurance Program Plan for the Waste Isolation Pilot Plant (WIPP) Project.[1] These target analytes must be determined in the waste before it can be shipped to the WIPP site near Carlsbad, NM, and subsequently buried.

This study focuses on three of the target volatile organic compounds (VOCs) expected to be found in sludge originating from Rocky Flats Plant (RFP) in Colorado. The RFP sludge is destined for the WIPP site. The sludge, classified as Type IV,[2] was generated at RFP by immobilizing oils and organic liquids that had been used during the manufacture of defense-related nuclear devices. The three VOCs that are of interest in this study are carbon tetrachloride, 1,1,1-trichloroethane, and Freon 113 (1,1,2-trichloro-1,2,2-trifluoroethane), which were widely used as degreasing agents at RFP during the machining of nuclear weapons. On the basis of historical knowledge of the sludge, it is highly probable that these three VOCs will be present at percent levels. Using traditional methods to analyze samples with high VOC levels would cause contamination of the analytical system and cross-contamination from sample to sample. In addition, the presence of both radioactive and hazardous components in the sludge classifies the sample as "mixed waste." Therefore, efforts were undertaken to identify a method for the determination of the three VOCs that is simple and generates a minimum amount of waste.

The RFP sludge consists of organic liquid wastes (organic solvents, degreasers, and cutting oils) mixed with calcium silicate (MicroCel E®) and small oil-absorbing stones (Oil Dri®) to form a grease or paste-like material. Since actual Type IV RFP radioactive sludge was not available for laboratory use at the onset of this study, we prepared a simulated sludge that was in accordance with the EG&G Internal Technical Report, <u>Properties and Simulation of Rocky</u>

Flats Waste Sludges.[3] See Appendix A of the Argonne National Laboratory Technical Report, Determination of PCBs in Rocky Flats Type IV Waste Sludge by Gas Chromatography/Electron Capture Detection,[4] for a detailed description of the preparation of Type IV simulated sludge.

The objective of this study is to evaluate three different techniques to analyze for high levels of the three VOCs in RFP Type IV sludge. These techniques are as follows:

- Static Headspace Gas Analysis Method. An adaptation of the EPA SW-846 screening method 3810 Headspace (Rev. 0, September 1986).[5]
- Methanol Extraction Method. An adaptation of the Contract Laboratory Program (CLP) method for high-level anaysis of volatile organics.[6]
- Ethylene Glycol Extraction Method. Also an adaptation of the CLP analysis method for volatile organics,[6] except that ethylene glycol is used as an extractant instead of methanol.

II. EXPERIMENTAL

A. Scope and Application

The methods in this report are being proposed for use in quantifying high concentrations (100 ppm to 2 percent) of three VOCs (carbon tetrachloride, 1,1,1-trichloroethane, and Freon 113) in RFP Type IV sludge. Therefore, the design of these methods did not stress low limits of quantitation. (Levels higher than 2 percent will be detected by these methods but quantitative accuracy will suffer at levels higher than 2 percent due to the limited linear range of the mass selective detector.) Because the field samples will be mixed waste, the methods were designed to be simple and to generate little or no additional mixed waste. The methods were developed on the premise that Type IV RFP sludge samples are expected to contain high levels of the three VOCs. The expectation of high levels of VOCs is based on historical information on how this particular waste stream was generated.

B. Summary of Methods

1. Static Headspace Gas Analysis Method

An aliquot of sludge is weighed and transferred to a vial. Internal standard (fluorobenzene) is added to each vial. The vial is heated, and a portion of the headspace gas is withdrawn with a syringe and analyzed by gas chromatography/mass spectrometry (GC/MS).

2. Methanol Extraction Method

An aliquot of sludge is weighed and transferred to a vial. Internal standard (fluorobenzene) and 5 mL of methanol are added to the vial. The sample is mixed, and an aliquot of the extract is analyzed by purge-and-trap GC/MS analysis.

3. Ethylene Glycol Extraction Method

An aliquot of sludge is weighed and transferred to a vial. Internal standard (fluorobenzene) and 5 mL of ethylene glycol are added to the vial. The sample is mixed, and an aliquot of the extract is analyzed by purge-and-trap GC/MS analysis.

C. Interferences

The use of plastic or rubber components was avoided since such materials out-gas organic compounds, which can become concentrated in the trap during the purge operation (Teflon® components are recommended). Before processing samples, the analyst should demonstrate daily, through the analysis of reagent blanks, that the entire analytical system is interference free.

Samples can be contaminated by diffusion of volatile organics (particularly chlorofluorocarbons and methylene chloride) through the sample container septum during shipment and storage. As a result, a field sample blank prepared from reagent water and carried through sampling and subsequent storage and handling can serve as a check on such contamination.

Contamination by carryover can occur whenever high-level and low-level samples are sequentially analyzed. To reduce carryover contamination, the sample syringe was rinsed out between samples with reagent water. Whenever a highly concentrated sample is encountered, it was followed by an analysis of reagent water. In some cases, the syringe may require a more thorough cleaning with detergent and water, and then drying at 105°C.

D. Apparatus and Materials

- Gas chromatograph--Hewlett Packard 5890 Series II.
- Mass Selective Detector--Hewlett Packard 5971 Series.
- Purge and Trap Device--Tekmar® Liquid Sample Concentrator LSC-2 (for methanol and ethylene glycol extraction methods).
- Capillary Column--J&W Scientific (Cat. No. 125-1334) 30-m length x 0.53 mm ID, phase DB624, film thickness 3.0 µm.
- Heated water bath capable of heating to 90°C (±5°C) (for static headspace gas

analysis method).

- Sartorius® laboratory balance capable of weighing to the nearest 0.01 g.
- Glass I-Chem® screw-cap vials (40 mL) with Teflon®-lined septas (for static headspace gas analysis method).
- Glass I-Chem® screw-cap vials (20 mL) with Teflon®-lined septas (for methanol and ethylene glycol extraction methods).
- Gas-tight syringe with gas sampling valve (for static headspace gas analysis method).
- Gas-tight syringe (100, 250, and 500 µL).

E. Reagents

- Methanol--Fisher® purge and trap grade, 99.9% purity, Lot 944518.
- Fluorobenzene--Chem Serv® (Westchester, PA), 99.0% purity, Lot 102-111A.
- Ethylene glycol--Baker Analyzed® Reagent, 99% purity, Lot H07624.
- Organic-free reagent water, as defined in Chapter One of Reference 5.

F. Procedure

Table 1 lists the instrumental conditions for the three methods evaluated in this study.

Table 1. Instrumental Conditions

Parameter	Static Headspace Method[a]	Methanol and Ethylene Glycol Methods
Purge and Trap Conditions		
Purge time	N/A	10 min (open tube)
Purge flow	N/A	~40 mL/min (helium)
Desorb time	N/A	3 min
Desorb temperature	N/A	195°C
Bake time	N/A	10 min
Bake temperature	N/A	220°C
Gas Chromatographic Conditions		
Column type	J&W Scientific DB624, 30 m x 0.53 mm ID, 3.0 µm film	J&W Scientific DB624, 30 m x 0.53 mm ID, 3.0 µm film
Carrier gas	Helium	Helium
Column flow	6 mL/min	6 mL/min
Total flow	250 mL/min	50 mL/min
Purge on	0 min	0.5 min
Purge off	22 min	0 min
Injection volume	100 µL (split)[b]	13 µL (splitless)[c]
Split ratio	20:1	N/A
Injection temperature	200°C	225°C
Detector temperature	250°C	250°C
Initial oven temperature	35°C	35°C
Initial time	7 min	7 min
Temperature program	35°C to 47°C at 3°C/min then 47°C to 130°C at 50°C/min and hold 9 min	35°C to 47°C at 3°C/min then 47°C to 130°C at 50°C/min and hold 9 min
Total time	22 min	22 min
Mass Spectrometric Conditions		
Open split interface temperature	250°C	250°C
Source temperature	250°C	250°C
Scan range	30 - 350 amu	33 - 350 amu
Scan rate	0.6 scans/sec	0.6 scans/sec
Solvent delay	1.6 min	2.75 min

[a] N/A indicates not applicable.

[b] Volume of headspace gas.

[c] Volume of extract added to 5 mL of water for the purge-and-trap method.

1. Static Headspace Gas Method

The steps in the static headspace method are as follows: Weigh approximately 1.0 g (measured to 0.01 g) of a sludge sample and transfer to a 40-mL vial. Add 50 µL of a 5% (w/v) fluorobenzene internal standard solution to the vial. Heat the vial to 90°C in a water bath for one-half hour. While the vial is at 90°C, withdraw 100 µL of the headspace gas with a gas-tight syringe and analyze immediately by direct injection into a GC/MS. See Table 1 for instrumental conditions.

a. Calibration

Preparation of a five-point calibration curve begins with preparing a modified simulated sludge. The simulated sludge was modified by omitting the three VOCs of interest, because these compounds were subsequently added at specific levels. One gram of modified simulated sludge was added to each of five 40 mL vials. See Table 2 for recommended standard concentrations and amounts of standards to be added to each vial. The 1-g spiked sludge portions (calibration standards) were prepared and analyzed by the same procedure as for 1-g sample portions (see Section II.F.1).

Table 2. Preparation of Five-Point Calibration Curve for Static Headspace Method

Calibration Level	Internal Standard Conc. (µg/mL)	Amount of Internal Standard Added (µL)	Internal Standard Conc. in Sludge (µg/g)	Standard Conc.[a] (µg/mL)	Amount of Standard Added (µL)	Standard Conc. in Spiked Sludge (µg/g)
1	50,000	50	2500	5000	20	100
2	50,000	50	2500	5000	100	500
3	50,000	50	2500	125,000	20	2500
4	50,000	50	2500	125,000	80	10,000
5	50,000	50	2500	125,000	200	25,000

[a] Standard solution containing carbon tetrachloride, 1,1,1-trichloroethane, and Freon 113.

b. Sample Analysis and Evaluation

Prior to and during the analysis of samples and standards, certain Quality Assurance Objectives (QAOs) must be met. The QAOs that apply to volatile organic analysis for the WIPP project are found in Section 13.0 of the TRU Waste Characterization Quality Assurance Program Plan.[1] The QAOs were used here as a measure of the performance of the method; however, due to the specific purpose of this method, namely to determine high levels of at least three VOCs, some of the QAOs are not applicable (e.g., method detection limits). See Section III for a more detailed discussion of the QAOs.

Instrument Tuning: To ensure that the system is properly tuned, a solution of bromofluorobenzene (BFB) is injected into the system and analyzed. The mass spectrum of the BFB solution must meet the criteria in Table 4 of SW-846 Method 8260.[5] (The GC/MS hardware may require some tuning adjustments in order to meet the criteria.)

Initial Calibration: A five-point calibration curve is prepared at concentrations that define the range of the method (see Table 2). The average relative response factor (RRF) is calculated and recorded for each compound. Then, the percent relative standard deviation (%RSD) for each compound is calculated from the RRFs. The average RRF and %RSD should meet criteria set by the QAOs.

Continuing Calibration: Once every 12 hours, a mid-point calibration standard is run. The RRF for each compound is calculated and recorded. The percent difference between the continuing calibration RRF and the initial calibration RRF is also calculated and recorded. The RRF of the continuing calibration and the percent difference should meet criteria set by the QAOs.

Statistical Analysis: Refer to SW-846 Method 8260[5] for calculation of RRFs, %RSD, percent difference, and sample concentrations.

Internal Standard: Quantitation is based on the area response of the characteristic ion of the internal standard compound and the compound being measured. (See Table 3 for a list of retention times and characteristic ions.)

Table 3. Retention Times and Characteristic Ion Mass-to-Charge Ratio (M/Z) for Static Headspace Method

Compound	Approximate Retention Time (min)	Characteristic Ion (M/Z)
Freon 113	2.9	101
1,1,1-Trichloroethane	7.4	97
Carbon Tetrachloride	7.9	117
Fluorobenzene (internal standard)	9.5	96

Examples of total ion chromatograms generated by the static headspace method are presented in Figs. 1-3. For Fig. 1, the three VOC standards were added to a vial and analyzed using the same procedure as for a complete sample except that the matrix was omitted. For Fig. 2, the matrix was present but the standards were omitted in order to determine whether any components in the matrix would interfere with the quantitation of the three VOCs. Finally, for Fig. 3, both the standards and matrix were included in order to generate a chromatogram of a typical sludge sample containing 2500 ppm of each of the three VOCs. The internal standard (fluorobenzene) was present in all chromatograms, and it has a retention time of approximately 10 min.

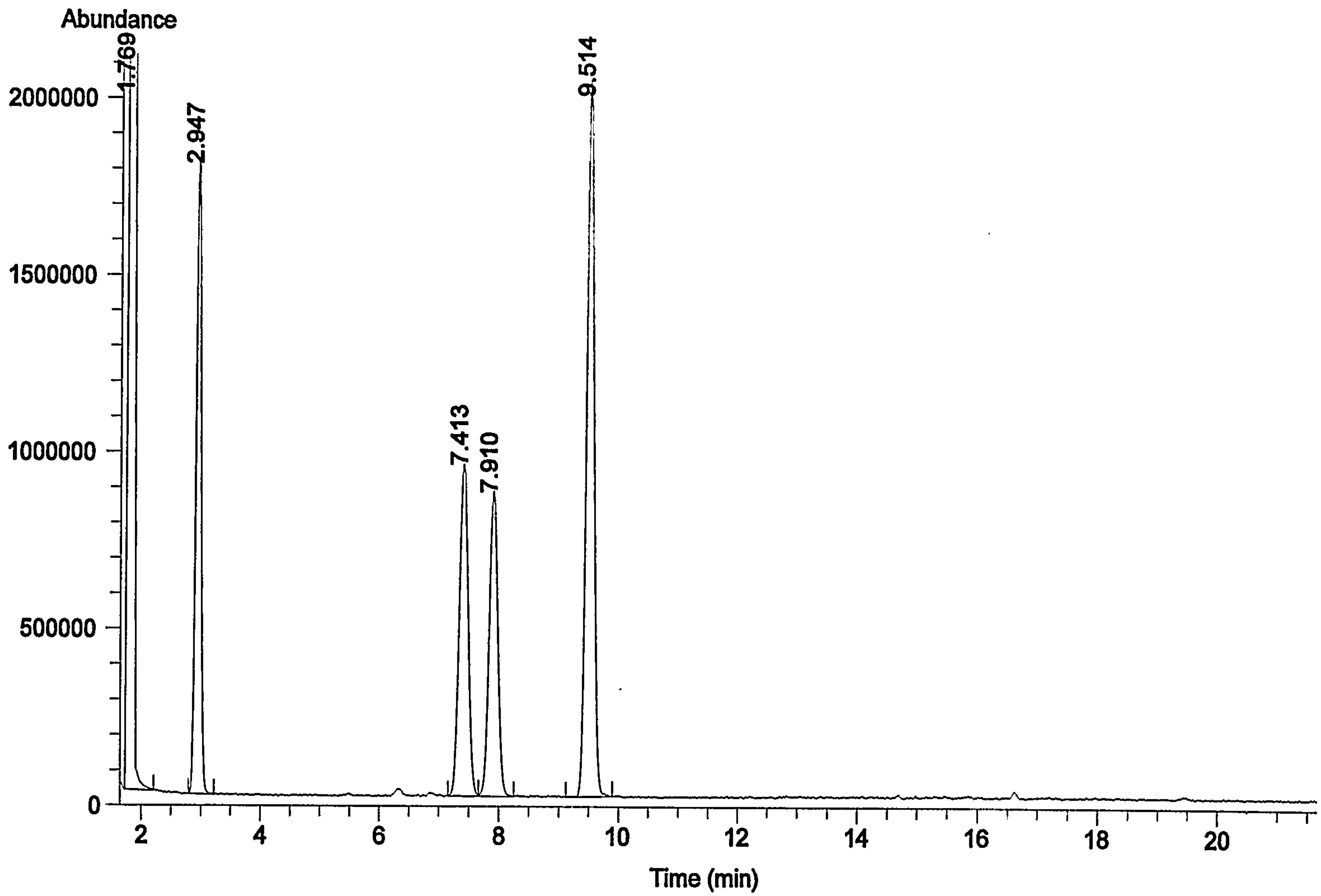

Figure1. Static Headspace Gas Method - Calibration Level 3 with No Sludge Matrix Present

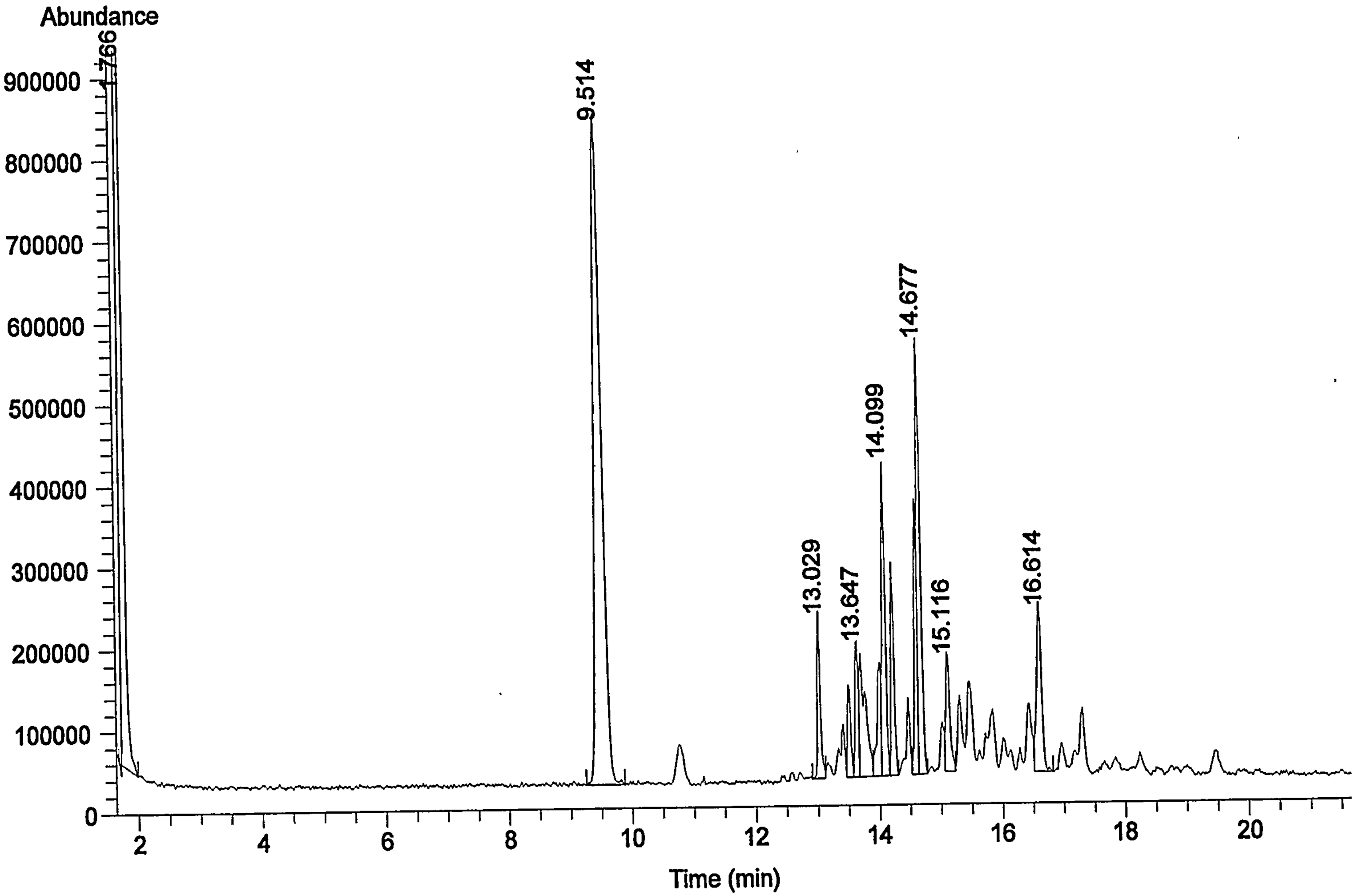

Figure 2. Static Headspace Gas Method - Blank Sludge (no standards added)

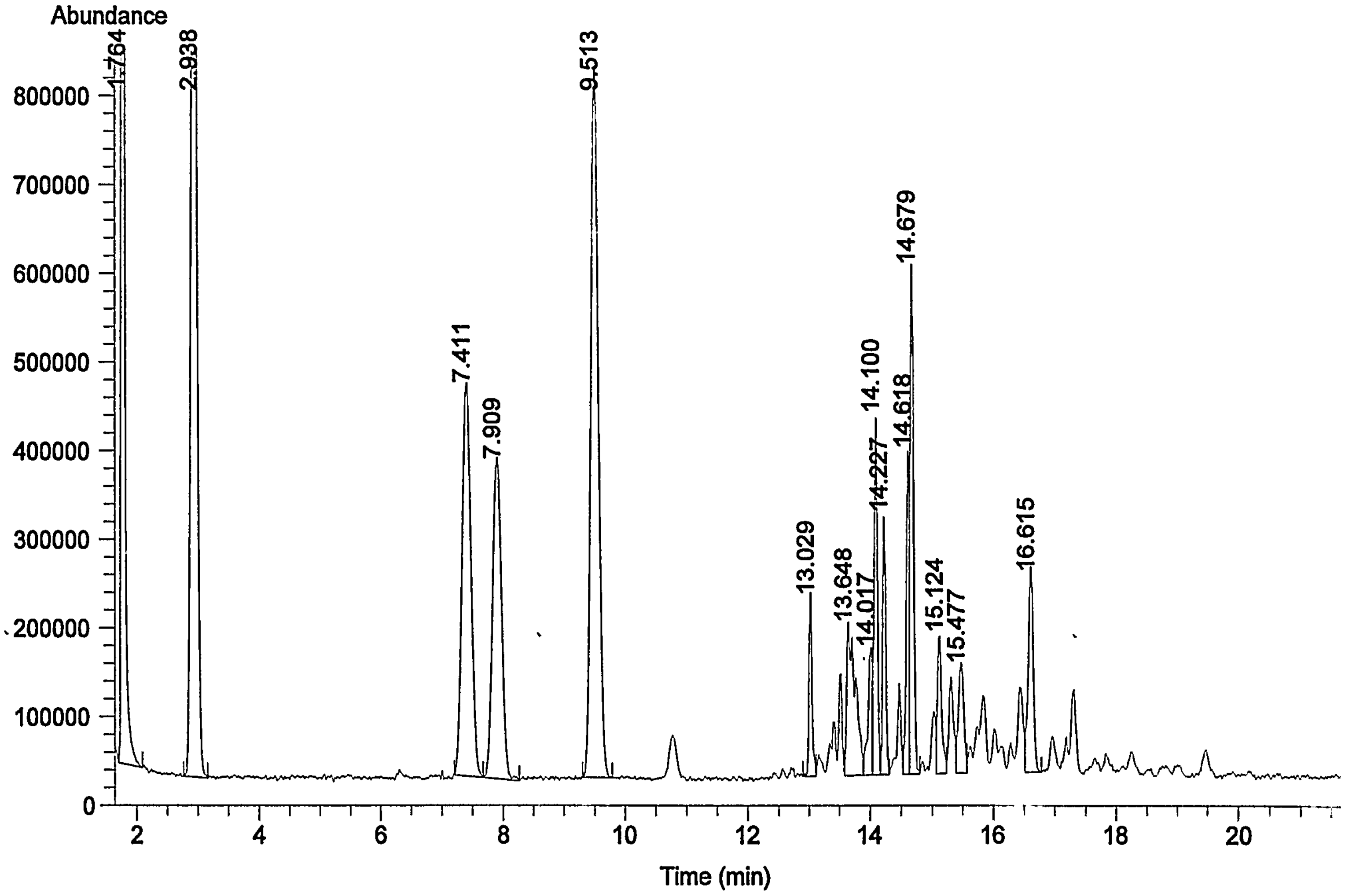

Figure 3. Static Headspace Gas Method - Calibration Level 3 with Sludge Matrix Present

2. Methanol Extraction Method

The steps in the methanol extraction method are as follows: Weigh approximately 1.0 g (measured to 0.01 g) of a sludge sample and transfer to a 20 mL vial. Add 25 µL of 125 µg/mL fluorobenzene internal standard solution and 5 mL of methanol to the vial. Vortex the vial for at least 30 s. Add 13 µL of the methanol extract to 5 mL of water in a purge-and-trap test tube. Analyze by purge-and-trap GC/MS. See Table 1 for instrumental conditions.

a. Calibration

A five-point calibration curve is prepared by adding 5 mL of water to each of five purge-and-trap test tubes. See Table 4 for the recommended standard concentrations and amounts of standards to be added to each tube. Each calibration standard is analyzed by purge-and-trap GC/MS.

Table 4. Preparation of Five-Point Calibration Curve for Methanol and Ethylene Glycol Extraction Methods

Calibration Level	Internal Standard Conc. (µg/mL)	Amount of Internal Standard Added (µL)	Final Internal Standard Conc. (µg/mL)	Standard Conc.[a] (µg/mL)	Amount of Standard Added (µL)	Final Standard Conc. (µg/mL)
1	125	25	0.625	5	25	0.025
2	125	25	0.625	25	25	0.125
3	125	25	0.625	125	25	0.625
4	125	25	0.625	500	25	2.50
5	125	25	0.625	1250	25	6.25

[a] Standard solution containing carbon tetrachloride, 1,1,1-trichloroethane, and Freon 113.

b. Sample Analysis and Evaluation

Prior to and during the analysis of samples and standards, certain Quality

Assurance Objectives (QAOs) must be met. The QAOs that apply to volatile organic analysis for the WIPP project are found in Section 13.0 of the TRU Waste Characterization Quality Assurance Program Plan.[1] The QAOs were used here as a measure of the performance of the method; however, due to the specific purpose of this method, namely to determine high levels of at least three VOCs, some of the QAOs are not applicable (e.g., method detection limits). See Section III for a more detailed discussion of the QAOs.

Instrument Tuning: To ensure that the GC/MS system is properly tuned, a solution of bromofluorobenzene (BFB) is injected into the system and analyzed. The mass spectrum of the BFB solution must meet the criteria in Table 4 of SW-846 Method 8260.[5] (The GC/MS hardware may require some tuning adjustments in order to meet the criteria.)

Initial Calibration: A five-point calibration curve is prepared at concentrations that define the range of the method (see Table 4). The average relative response factor (RRF) is calculated and recorded for each compound. Then, the percent relative standard deviation (%RSD) for each compound is calculated from the RRFs. The average RRF and %RSD should meet criteria set by the QAOs.

Continuing Calibration: Once every 12 hours, a mid-point calibration standard is run. The RRF for each compound is calculated and recorded. The percent difference between the continuing calibration RRF and the initial calibration RRF is also calculated and recorded. The RRF of the continuing calibration and the percent difference should meet criteria set by the QAOs.

Statistical Analysis: Refer to SW-846 Method 8260[5] for calculation of RRFs, %RSD, percent difference, and sample concentrations.

Internal Standard: Quantitation is based on the area response of the characteristic ion of the internal standard compound and the compound being measured. (See Table 5 for a list of retention times and characteristic ions.)

Table 5. Retention Times and Characteristic Ion Mass-to-Charge Ratio (M/Z) for Methanol Extraction Method

Compound	Approximate Retention Time (min)	Characteristic Ion (M/Z)
Freon 113	3.4	101
1,1,1-Trichloroethane	8.3	97
Carbon Tetrachloride	8.8	117
Fluorobenzene (internal standard)	10.4	96

Examples of total ion chromatograms generated by the methanol extraction method are presented in Figs. 4-6. Figure 4 is a chromatogram of calibration standard level three. For Fig. 5, the matrix was present, but the standards were omitted in order to determine whether any components in the matrix would interfere with the quantitation of the three VOCs. For Fig. 6, both the standards and matrix were included in order to generate a chromatogram of a typical sludge sample containing 2500 ppm of each of the three VOCs. The internal standard (fluorobenzene) was present in all chromatograms, and it has a retention time of approximately 10 min.

3. Ethylene Glycol Extraction Method

The procedure for the ethylene glycol extraction method is identical to the methanol extraction method except that ethylene glycol is used as an extractant instead of methanol. Preparation of the calibration standards is identical to the procedure for preparing the methanol extraction calibration standards (i.e., all standards are prepared in methanol, not ethylene glycol). In addition, all of the instrumental parameters are also the same (refer to Section II.F.2 for procedural details).

Examples of total ion chromatograms generated by the ethylene glycol extraction method are presented in Figs. 4, 7, and 8. As stated above, Fig. 4 is a chromatogram of calibration standard level three. For Fig. 7, the matrix was present, but the standards were omitted in order to determine whether any components in the matrix would interfere with the quantitation of the three VOCs. For Fig. 8, both the standards and matrix were included in order to generate a chromatogram of a typical sludge sample containing 2500 ppm of each of the three VOCs of interest. The internal standard (fluorobenzene) was present in all chromatograms, and it has a retention time of approximately 10 min.

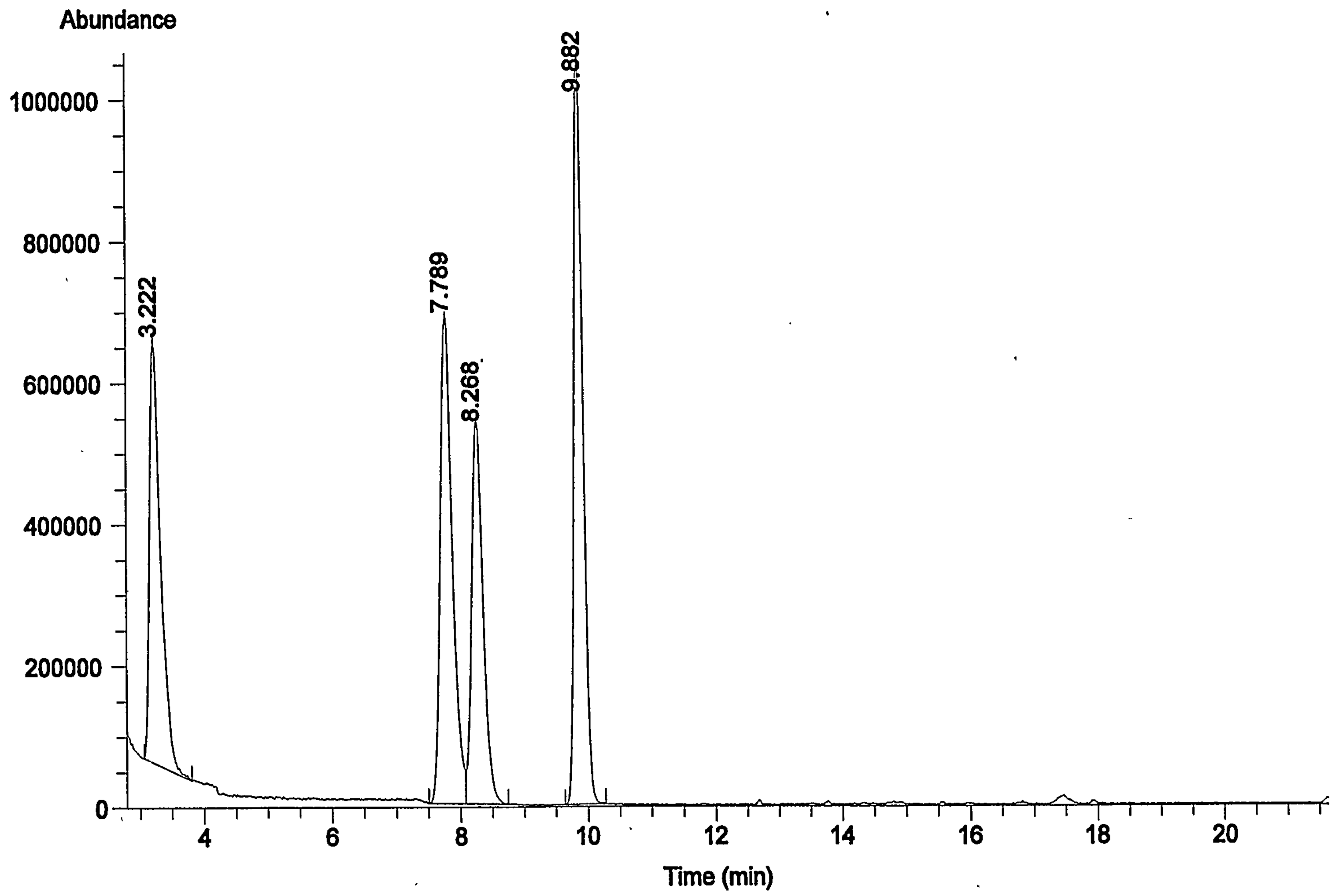

Figure 4. Methanol and Ethylene Glycol Methods - Calibration Level 3 with No Sludge Matrix Present

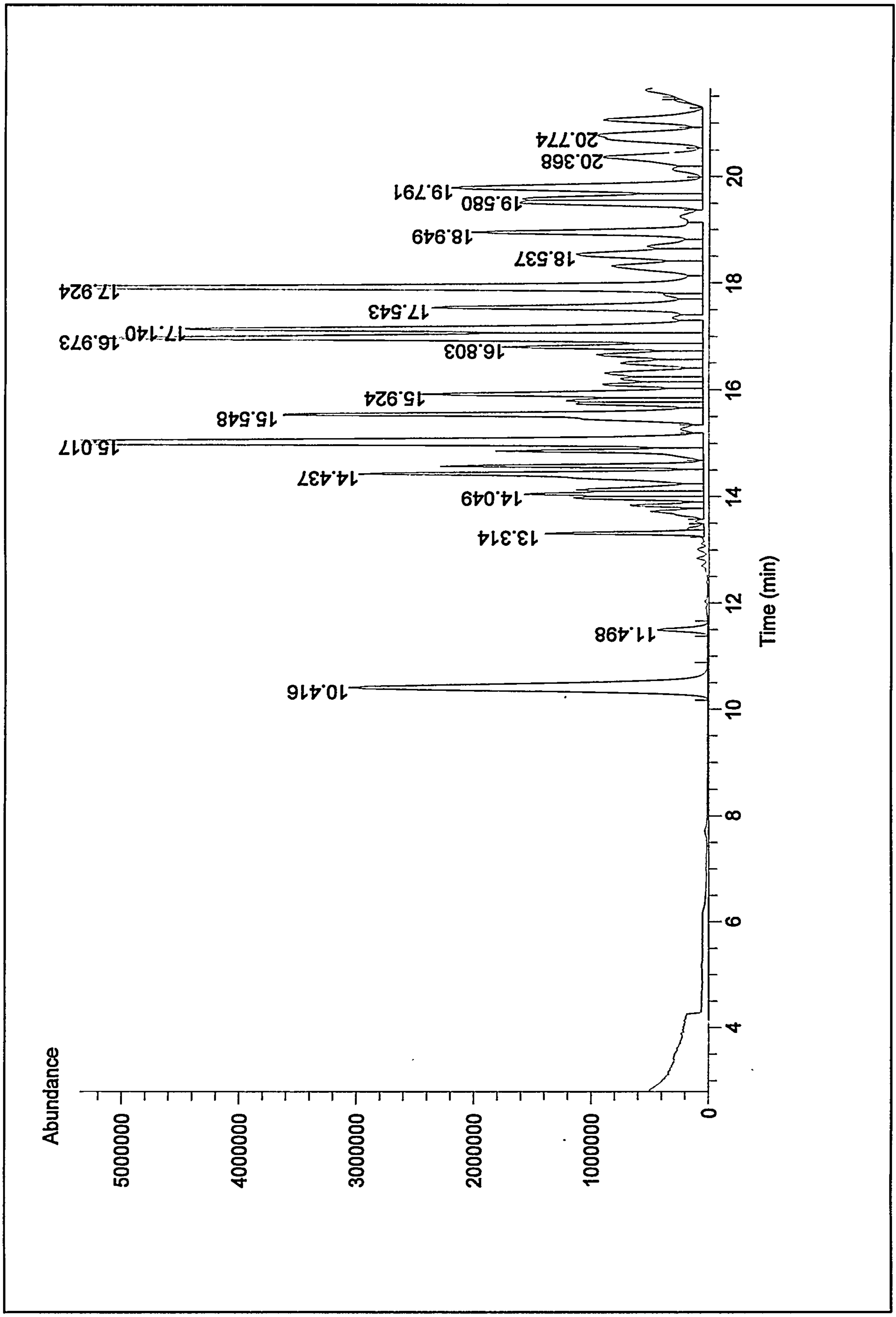

Figure 5. Methanol Extraction Method - Blank Sludge (no standards added)

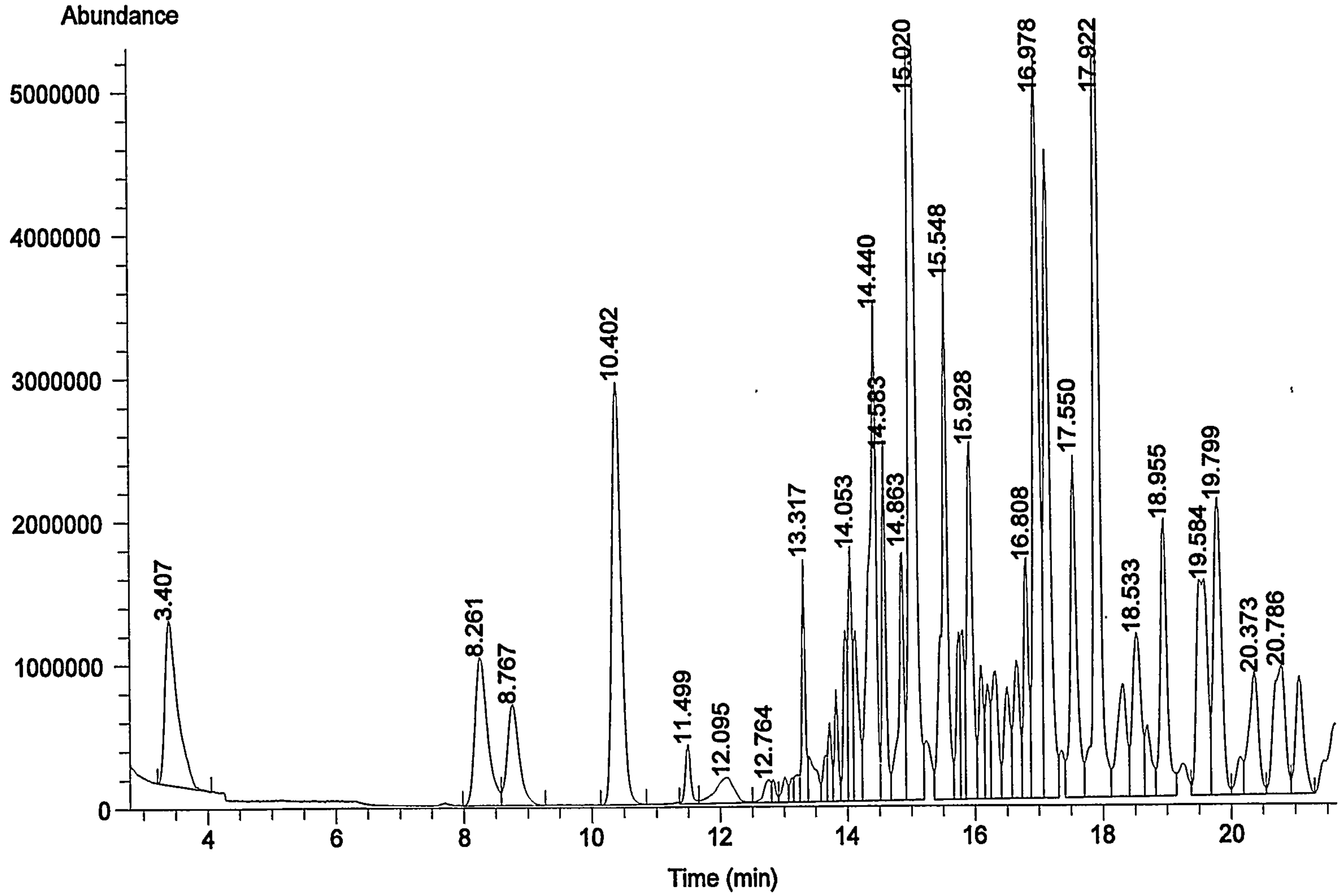

Figure 6. Methanol Extraction Method - Spiked Sludge (2500 ppm)

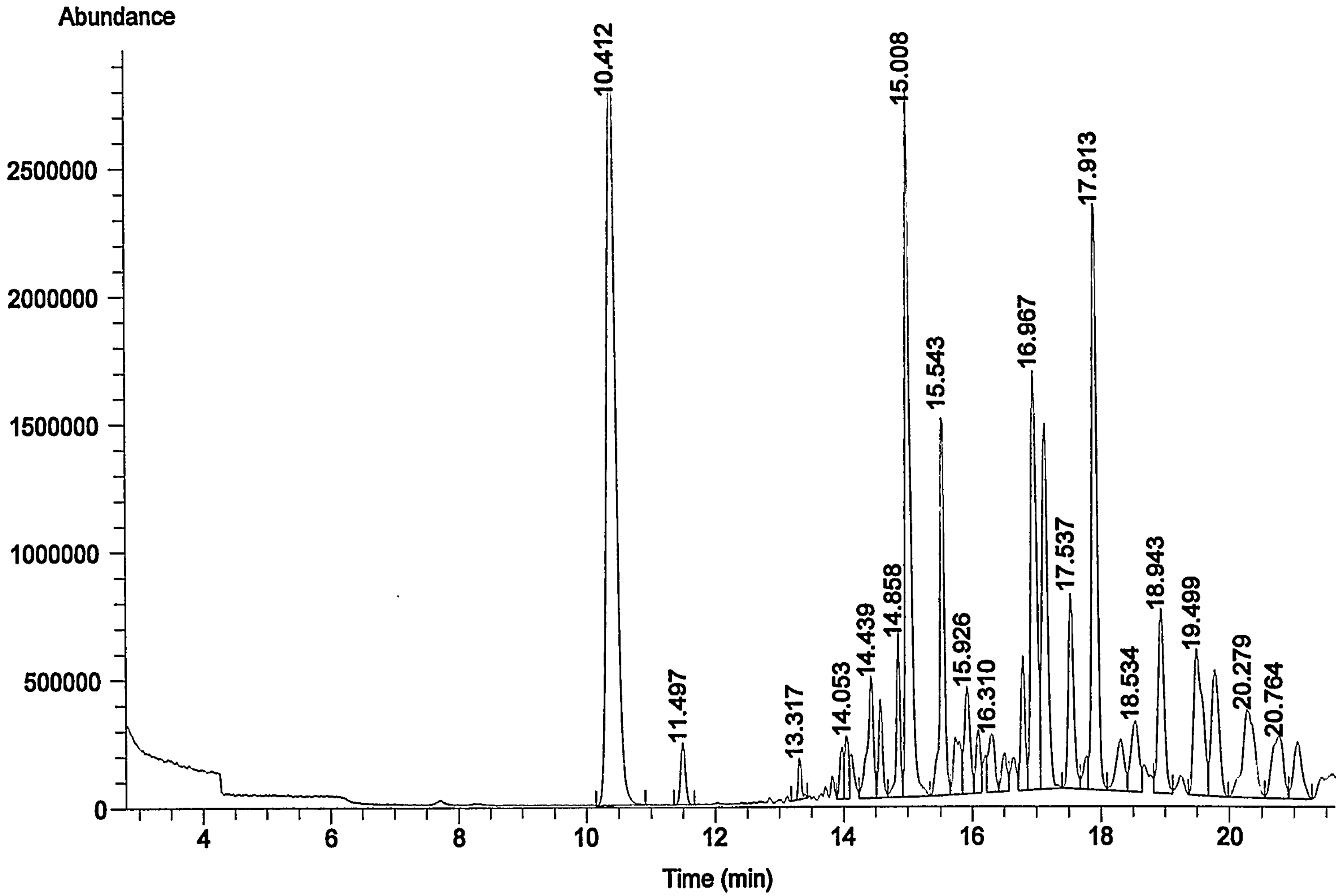

Figure 7. Ethylene Glycol Extraction Method - Blank Sludge (no standards added)

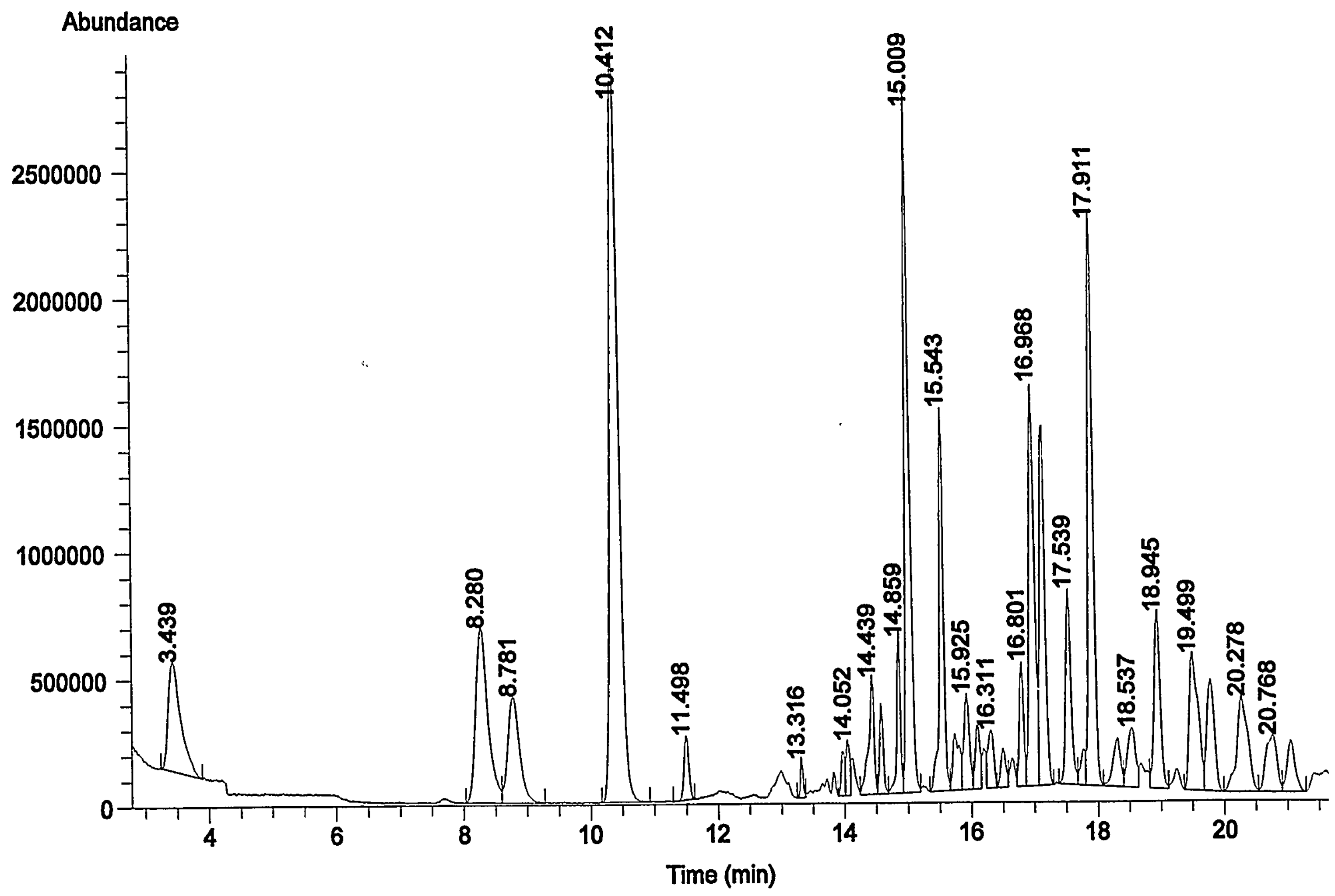

Figure 8. Ethylene Glycol Extraction Method - Spiked Sludge (2500 ppm)

III. RESULTS AND DISCUSSION

The proposed methods were applied to simulated RFP Type IV sludge, which consists of an organic liquid mixed with MicroCel E® (calcium silicate) and Oil Dri®. Three of the components that are expected to makeup a relatively large portion of the sludge are VOCs for which analysis is required prior to shipment of the waste sludge to the WIPP site. The three VOCs were added to the sludge in known amounts, and the performance of the methods was checked. The QAOs for total VOC analysis[1] are used here as a measure of the performance of the proposed methods.

A. Static Headspace Method

A five-point calibration curve was prepared from analytical data generated with the static headspace gas analysis method. The RRFs and %RSDs are given in Table 6.

Table 6. Relative Response Factors and Percent Relative Standard Deviation for Static Headspace Calibration Curve

Calibration Level	Freon 113	1,1,1-Trichloroethane	Carbon Tetrachloride
Level 1 (100 ppm)	0.644	0.373	0.348
Level 2 (500 ppm)	0.565	0.362	0.334
Level 3 (2500 ppm)	0.473	0.355	0.331
Level 4 (10,000 ppm)	0.418	0.340	0.317
Level 5 (25,000 ppm)	0.248	0.266	0.243
Average RRF	0.470	0.339	0.315
%RSD	32	13	13

According to the QAOs, the average RRF must be at least 0.300 (0.250 for bromoform) for System Performance Check Compounds (SPCC).[5] There are five SPCCs, but the three VOCs of interest do not coincide with any of the five; therefore, this criterion is not applicable to this set of analytes. The QAOs also require that the %RSD be less than 30% for low level methods. As shown in Table 6, the %RSDs for 1,1,1-trichloroethane and carbon tetrachloride were well below the minimum requirement; however, Freon 113 was slightly over the minimum %RSD. The higher %RSD for Freon 113 is likely caused by a limit in the linear range of the mass selective detector for this compound. Table 6 also shows a marked decrease in RRF between level 4 (1% standard) and level 5 (2.5% standard). The minimum 30 %RSD requirement can be met for Freon 113 by narrowing the working range of the calibration curve for this compound. This may not be critical to the performance of the method, since prescribed action limits for these VOCs will likely be set for less than 1% of the VOCs. Additionally, the calibration curve for Freon 113 exceeded the 30% RSD requirement by only 2%. This calibration curve covers a 250-fold concentration range, as compared to only a 20-fold concentration range for traditional VOC methods.

The method detection limit was determined by analyzing eight 1-g simulated sludge samples that were spiked at 100 ppm with each of the three VOCs. The eight runs were also used to determine the precision and accuracy of the method. See Table 7 for MDL, precision (%RSD), and accuracy (percent recovery) results for the static headspace gas analysis method.

Table 7. Detection Limit, Precision, and Accuracy for Static Headspace Method

Replicate #	Freon 113 (ppm)	1,1,1-Trichloroethane (ppm)	Carbon Tetrachloride (ppm)
1	108	99	96
2	68	74	70
3	95	92	91
4	86	93	89
5	99	97	95
6	125	105	106
7	109	106	108
8	84	93	94
Average	97	95	94
%RSD	18	11	12
% Recovery	97	95	94
MDL[a]	53	30	35

[a] Method Detection Limit as defined in Ref. 7 is MDL = $t_{(\eta-1,1-\alpha=0.99)}$*s, where $t_{(\eta-1,1-\alpha=0.99)}$ is the t distribution value appropriate to a 99% confidence level and a standard deviation estimate with η - 1 degrees of freedom, and s is the standard deviation of replicate measurements.

According to the QAOs, the precision of the method must be ±50% for Freon 113, ±33% for 1,1,1-trichloroethane, and ±30% for carbon tetrachloride. Table 7 shows that the precision of this method (%RSD) easily meets the criteria for all three VOCs. Since this method was proposed for the determination of high levels of VOCs, the MDLs for low level determinations listed in the TRU Waste QAPP[1] are not applicable; however, our initial goal was to achieve MDLs less than 100 ppm for all three VOCs.

The QAOs for accuracy are expressed as percent recovery and must be 60-150% for Freon 113, 52-162% for 1,1,1-trichloroethane, and 70-140% for carbon tetrachloride. With the static headspace gas method, only moderate absolute recoveries were expected; therefore, the calibration curve for the static headspace method was prepared and analyzed in the same way that a field sample would be analyzed. By preparing the curve in this way, we are able to account for any VOC losses encountered that are inherent in the procedure. Hence, repeatability of the results is the major factor affecting accuracy for the static headspace method, and repeatability of the results is expressed in Table 7 as %RSD.

B. Methanol Extraction Method

A five-point calibration curve was prepared for the analytical data obtained according to the CLP Method for High Level Analysis of Volatile Organics.[6] The RRFs and %RSDs are given in Table 8.

Table 8. Relative Response Factors and Percent Relative Standard Deviation for Methanol Extraction Calibration Curve

Calibration Level	Freon 113	1,1,1-Trichloroethane	Carbon Tetrachloride
Level 1 (100 ppm[a])	0.212	0.468	0.509
Level 2 (500 ppm[a])	0.234	0.483	0.501
Level 3 (2500 ppm[a])	0.212	0.483	0.492
Level 4 (10,000 ppm[a])	0.221	0.442	0.473
Level 5 (25,000 ppm[a])	0.225	0.447	0.489
Average RRF	0.221	0.465	0.493
%RSD	4	4	3

[a]Equivalent concentration in sludge.

According to the QAOs, the average RRF must be at least 0.300 (0.250 for bromoform) for the SPCC.[5] There are five SPCCs, but the three VOCs of interest do not coincide with any of the five; therefore, this criterion is not applicable to this set of analytes. The QAOs also require that the %RSD be less than 30%. The %RSD criterion was easily met for all three compounds.

The method detection limit was determined by analyzing eight 1-g simulated sludge samples that were spiked at approximately 100 ppm with each of the three VOCs. The eight runs were also used to determine the precision and accuracy of the method. See Table 9 for MDL, precision (%RSD), and accuracy (percent recovery) results for the methanol extraction method.

Table 9. Detection Limit, Precision, and Accuracy for Methanol Extraction Method

Replicate #	Freon 113 (ppm)	1,1,1-Trichloroethane (ppm)	Carbon Tetrachloride (ppm)
1	139	128	86
2	141	133	88
3	131	127	86
4	131	124	86
5	141	132	89
6	143	128	87
7	142	127	87
8	134	125	91
Average	138	128	88
%RSD	4	3	2
% Recovery	86	94	91
MDL[a]	15	10	6

[a] Method Detection Limit as defined in Ref. 7 is MDL = $t_{(\eta-1,1-\alpha = 0.99)}$*s, where $t_{(\eta-1,1-\alpha = 0.99)}$ is the t distribution value appropriate to a 99% confidence level and a standard deviation estimate with η - 1 degrees of freedom, and s is the standard deviation of replicate measurements.

According to the QAOs, the precision of the method must be ±50% for Freon 113, ±33% for 1,1,1-trichloroethane, and ±30% for carbon tetrachloride. The precision of this method

(%RSD) easily meets the criteria for all three VOCs. The QAOs for accuracy are expressed as percent recovery and must be 60-150% for Freon 113, 52-162% for 1,1,1-trichloroethane, and 70-140% for carbon tetrachloride. The accuracy of this method also meets the criteria for all three VOCs. Since this method was proposed for the determination of high levels of VOCs, the MDLs listed in the TRU Waste QAPP[1] are not applicable; however, our initial goal was to achieve MDLs less than 100 ppm for all three VOCs.

C. Ethylene Glycol Extraction Method

The same five-point calibration curve that was prepared for the methanol extraction method was used for the ethylene glycol extraction method. The same RFs and %RSDs apply that were given in Table 8.

After several attempts were made to optimize the method, it became obvious that ethylene glycol was not a feasible extractant for this matrix type. The ethylene glycol and the simulated sludge formed multiple phases upon mixing, and the mixture was very viscous and particulate laden, making it difficult to withdraw a portion of the extract for analysis. (In contrast, particulates in the methanol extract tended to settle to the bottom rather quickly because of the lower viscosity of methanol.) The difficulty encountered in working with this extract did not meet our initial method criterion of being simple to perform, and preliminary method accuracy did not meet WIPP QAPP criteria. Ethylene glycol was initially proposed as an extractant because it is not a listed hazardous compound.

IV. CONCLUSION

In summary, both the static headspace gas analysis method and the methanol extraction method performed well for the determination of high levels (100 ppm to 2.5% levels) of the three VOCs of interest in RFP Type IV sludge. Table 10 summarizes the performance of the two methods. The use of ethylene glycol as an extractant was found to be incompatible with Type IV sludge.

Table 10. Comparison of the Performance of the Static Headspace Gas Analysis Method and the Methanol Extraction Method

	Freon 113		
Method Performance	QAO	Static Headspace	Methanol Extraction
MDL	N/A	53	15
%RSD	±50	18	4
%Recovery	60-150	97	86

	1,1,1-Trichloroethane		
Method Performance	QAO	Static Headspace	Methanol Extraction
MDL	N/A	30	10
%RSD	±33	11	3
%Recovery	52-162	95	94

	Carbon Tetrachloride		
Method Performance	QAO	Static Headspace	Methanol Extraction
MDL	N/A	35	6
%RSD	±30	12	2
%Recovery	70-140	94	91

The methanol extraction method demonstrated superior performance regarding MDLs and precision. Both methods performed nearly equivalently on accuracy. The major advantages that the static headspace method has over the methanol extraction method are that it generates no additional mixed waste and requires no additonal glassware. Both methods are simple to perform, and either method is more than adequate for the intended purpose, which is to determine high levels of VOCs in Type IV sludge. It is recommended that WIPP management set action limits for this sludge type, whereby if a particular sludge sample exceeded such limits, then additional testing of the sample for the full suite of VOC analytes would not be required. After action limits have been set, then QAOs applicable to this analysis type can be set. Implementation of either of these methods would eliminate the risk of contaminating traditional VOC analytical systems and is expected to eliminate the need, in most cases, for highly sensitive and costly analyses for this unique matrix. Additionally, because both methods use mass spectrometric detection, the presence and identification of other VOCs, in addition to the three investigated here, would be possible along with estimated quantitation of those VOCs.

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