



# Detection of petroleum-contaminated soils using EQUILIBRIUM HEADSPACE and METHANOL EXTRACTION

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## Introduction

Petroleum spills and leaking underground storage tanks comprise a significant portion of remediation projects. Soil removal and disposal is determined based on the contaminants and concentrations present. Specific target analytes are associated with this type of contamination. A number of these compounds are classified as volatile organics and are used to assess the severity of the contamination, whether remediation is required, and if necessary, the mode of disposal. The analytical technique used must accurately identify these components over a wide range of concentrations.

Volatile organic compounds in soils can be determined using the analytical EPA Method 8260, "Volatile Organic Compounds by Gas Chromatography/Mass Spectrometry (GC/MS)." <sup>(1)</sup> GC/MS adds another dimension to the analysis helping to ensure positive identification.

There are a number of methods that can be used to extract volatile organics from soil samples. EPA method 5035 is a purge-and-trap technique for the determination of low-level volatile organic compounds (VOCs) in soils. EPA method 5030 is a purge-and-trap technique for the analysis of high concentration VOCs in soils using methanol (MeOH) extracts. EPA method 5021 is a general purpose method for the determination of VOCs in soils using equilibrium headspace. Method 5021 is not restricted by the concentration limitations imposed on the two purge-and-trap methods.

Methanol extraction is a technique used in the analysis of VOCs. "...MeOH extraction can be a far more robust method of recovering VOCs from soil, especially for analytes with high octanol-water partitioning coefficients and matrices with organic carbon, than methods relying solely on vapor partitioning." <sup>(2)</sup> However, this extraction technique introduces a dilution factor, which can affect the ability to detect the analytes of interest. This application brief demonstrates the effective use of methanol extraction, equilibrium headspace sample introduction, and mass spectrometry detection for low-level VOC determinations.

## Summary

Typically, a 50 to 100- $\mu$ L aliquot of a methanol-extracted soil sample is added to 5 mL of deionized water for purging using method 5030. This introduces a dilution factor, which results in elevated detection limits,

making the technique only suitable for high level determinations. Alternatively, a headspace technique using 1 mL of methanol with 4 mL of deionized water results in increased sensitivity, eliminating the need for additional low-level analyses.

## Experiment and Conditions

One mL of methanol extract containing the analytes of interest is added to a 22-mL headspace vial containing 4 mL of deionized water. The vial is placed into the HS 40XL headspace sampler and thermostated using the conditions listed in Table 1. The vaporized analytes in the vial's headspace are transferred directly onto the GC column for chromatographic separation and detection using the Perkin-Elmer AutoSystem™ XL Gas Chromatograph interfaced to the Perkin-Elmer TurboMass™ Mass Spectrometer. Tables 2 and 3 contain the column and GC/MS conditions used to perform this application.

Table 1. Headspace conditions

Perkin-Elmer HS 40XL Equilibrium Headspace Sampler			
Carrier Gas	Helium	Transfer Line Temp.	100°C
Carrier Pressure	10 psi	Thermostating Time	10 min
Sample Shaker	On	Pressurization Time	0.5 min
High Pressure Sampling	35 psi	Injection Time	0.35 min
Oven Temperature	75°C	Withdrawal Time	0.4 min
Needle Temperature	80°C	Backflush	Off

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### System Performance

After demonstrating adequate system performance by analyzing an aliquot of Bromofluorobenzene (BFB) and meeting method 8260 criteria, a calibration curve must be performed.

### Calibration Standards

A minimum of five concentration calibration standards are prepared and analyzed using analytical conditions identical to those used for samples. One of the concentrations should be at a concentration near, but above, the method detection limit. The remaining concentrations should bracket the expected real sample concentration range, but must not exceed the working range of the GC/MS system. All standards must contain each analyte targeted for detection by this method. The internal standard technique is used to generate Response Factors (RFs). RFs are calculated for each compound relative to the nearest internal standard. The RF is calculated as follows:

$$RF = (A_{(x)}C_{(is)}) / (A_{(is)}C_{(x)})$$

where:

$A_{(x)}$  = Area of the characteristic ion for the compound being measured.

$A_{(is)}$  = Area of the characteristic ion for the specific internal standard.

$C_{(is)}$  = Concentration of the specific internal standard.

$C_{(x)}$  = Concentration of the compound being measured.

These *Relative Response Factors* (RRFs) are used to calculate the average RRF for every compound. The percent relative standard deviation (%RSD) is calculated using the average RRFs from the initial calibration. In order to evaluate the integrity of the calibration, the %RSD for each compound should be less than 15% and the minimum mean RF must be greater than 0.10. Table 4 lists the Initial Calibration Results for the target analytes and surrogate (Surr) compounds. The average RRF for each compound is well above the minimum 0.10 method criteria and the %RSDs are below the 15% maximum threshold level. **In all cases, the %RSD and mean RF was compliant with the method guidelines.**

**Table 2. Gas chromatographic conditions**

Perkin-Elmer AutoSystem XL Gas Chromatograph	
Oven Times and Temperatures:	
Initial	40°C for 1 min
Ramp rate	25°C/min to 220°C
Final	220°C for 6.4 min
Total Run Time	14.6 min
Column	DB-624 60 m x 0.32 mm ID, 1.8 µm film
Injector	None

**Table 3. Mass spectrometer conditions**

Perkin-Elmer TurboMass Mass Spectrometer					
EI Source		Mass Spec Settings		Scan Rate	
Electron Energy	70	LM Resolution	17.7	Range	35 amu – 300 amu
Emission	200	HM Resolution	13.7	Scan Time	0.3 sec
Repeller	1.2	Ion Energy	2.7	Inter-Scan Time	0.15 sec
Lens 1	13	Ion Energy Ramp	1.0		
Lens 2	118	Multiplier	420		
Source Temp.	175°C				

**Table 4. Initial calibration results**

Compound	AVG RF	% RSD
Dibromofluoromethane (Surr)	0.265	7.48
Toluene-d8 (Surr)	2.021	6.06
4-Bromofluorobenzene (Surr)	0.393	9.37
Methyl-tert-butyl ether (MTBE)	0.440	11.74
Benzene	1.305	7.11
Toluene	2.638	10.88
Ethylbenzene	2.536	9.63
p/m-Xylene	1.952	7.16
o-Xylene	1.596	9.77
1,3,5-Trimethylbenzene	3.612	9.24
1,2,4-Trimethylbenzene	2.977	9.87
Naphthalene	0.299	8.51

Table 5 displays the five standard concentrations analyzed using the aforementioned conditions along with the calculated analytical results. The concentrations presented reflect the calculated levels based on a 1 g:1 mL, soil:MeOH ratio. The agreement between known and analytically determined concentrations is excellent.

#### Detection Limits

Detection limits are calculated based on a minimum of three analyses of a standard containing the analytes of interest at an approximate concentration three to five times the estimated detection limit. The average and standard deviation for each analyte is calculated and the *t*-statistic applied. The resulting detection limit represents the minimum analyte concentration measured and reported with 99% confidence that the concentration is greater than zero. Table 6 lists the results of such a determination. A 20- $\mu\text{g}/\text{kg}$  standard was analyzed seven times. The results indicate a detection limit for each analyte at approximately 10 ppb.

**Table 5. Known and calculated concentrations based on a 1:1 methanol/soil extraction**

Compounds	Calibration Standards				
	20 ( $\mu\text{g}/\text{kg}$ )	50 ( $\mu\text{g}/\text{kg}$ )	100 ( $\mu\text{g}/\text{kg}$ )	150 ( $\mu\text{g}/\text{kg}$ )	200 ( $\mu\text{g}/\text{kg}$ )
Pentafluorobenzene (IS)	100	100	100	100	100
1,4-Difluorobenzene (IS)	100	100	100	100	100
Chlorobenzene-d5 (IS)	100	100	100	100	100
1,4-Dichlorobenzene-d4 (IS)	100	100	100	100	100
Dibromofluoromethane (Surr)	22.3	53.6	97.9	131	192
Toluene-d8 (Surr)	21.6	51.2	95.9	138	203
4-Bromofluorobenzene (Surr)	25.4	53.6	90.0	126	182
Methyl-tert-butyl ether (MTBE)	24.0	56.7	85.9	141	173
Benzene	22.4	54.2	90.3	144	187
Toluene	22.8	54.2	87.8	145	186
Ethylbenzene	22.5	52.8	88.0	150	188
p/m-Xylene*	43.0	1.7	181	297	384
o-Xylene	22.6	53.5	89.0	146	187
1,3,5-Trimethylbenzene	22.6	51.7	87.5	149	194
1,2,4-Trimethylbenzene	22.8	52.1	87.6	149	190
Naphthalene	22.6	51.3	90.1	144	197

\* Concs. represent both analytes

**Table 6. Detection limit results based on 7 replicate analyses of a 20- $\mu\text{g}/\text{kg}$  standard**

Compound	Method Detection Limits ( $\mu\text{g}/\text{kg}$ )		
	Average	SD	MDL
Methyl-tert-butyl ether (MTBE)	23.04	3.13	9.84
Benzene	21.33	2.38	7.47
Toluene	20.58	1.86	5.84
Ethylbenzene	21.49	1.73	5.44
p/m-Xylenes	41.27	3.35	10.54
o-Xylene	21.42	1.54	4.83
1,3,5-Trimethylbenzene	22.35	2.25	6.93
1,2,4-Trimethylbenzene	22.54	1.97	6.20
Naphthalene	31.11	2.68	8.42

## Conclusions

The data presented here demonstrate compliance with some of the more critical method acceptance criteria. In addition, this technique offers increased sensitivity for methanol-extracted soils, thereby eliminating additional low-level analyses. In an article comparing sample preparation methods for VOCs in soil samples, Alan Hewitt, of the U.S. Army Cold Regions Research and Engineering Laboratory, states, "When matrix interferences are expected or identified, MeOH extraction should be the method of choice. If MeOH extraction is not used, then it should be recognized that in comparison, most alternative procedures will result in lower quantitative recoveries."<sup>(2)</sup> Due to the limitations associated with large volumes of MeOH and the use of purge and trap, this technique has been restricted to the determination of high concentrations only. Using equilibrium headspace, VOCs can be determined over a wider range of concentrations and soil types using the same method and equipment. Furthermore, unlike purge-and-trap methods, headspace causes no equipment contamination and so lends itself to a wide range of concentrations in the same analytical run.

## Acknowledgments

The data presented here were generated and compiled by David Turriff, Ph.D., David Fountain, and Nils Melberg, En Chem, Inc., 1241 Bellevue St., Green Bay, WI 54302. Many thanks for their continued support.

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Order No. D-5877

September 1998

KG0998005

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