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Comparison of methanol and tetraglyme as extraction solvents for determination of volatile organics in soil

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The abilities of methanol and tetraglyme to extract chloroform, benzene, toluene, and tetrachloroethylene from vapor-contaminated soils are directly compared. Comparisons are made both with respect to process kinetics and analyte recovery using an extraction procedure based on equilibration on a wrist-action shaker and determination using a purge-and-trap GC/MS. An equilibration period of 10 minutes is recommended for extraction using either methanol or tetraglyme. In all cases methanol was as good as or better than tetraglyme with respect to analyte recovery. This was even the case for soils contaminated with an oily residue. While commercial methanol and tetraglyme both contain measurable levels of volatile aromatics, simple rotary evaporation was successful in removing these contaminants to levels below detection limits for tetraglyme. Thus, for cases where very small amounts of these contaminants must be detected, degassed tegraglyme would be superior. Overall, however, methanol is considered the best choice for extraction of volatile organics where subsequent analysis is to be conducted by purge-and-trap GC/MS.

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PREFACE

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INTRODUCTION

Background

Over the past several years, the degree to which groundwater in the United States has become contaminated with volatile organics has been increasingly recognized. To provide corrective action, the first step in each case is to locate the source of the contamination. In many cases, the source has proven to be soil contaminated with solvents from spills or leakage from underground storage tanks. To determine the levels of soil contamination, a reliable method is needed to determine soil volatiles.

The most important volatile contaminants from a human health standpoint are the aromatic hydrocarbons, such as benzene and toluene, and the halocarbons, such as carbon tetrachloride, trichloroethylene, and tetrachloroethylene. Because of the nature of these components and the likelihood that a number of different chemicals will be present simultaneously, the analytical method of choice has generally relied on gas chromatography as the determinative step. The gas chromatographic (GC) column effluents have been detected with either mass spectrometry (EPA 1984a) or a combination of a photoionization detector for aromatics (EPA 1984b) and a Hall detector for halocarbons (EPA 1984c).

The major question that has remained is which is the best method to quantitatively remove the volatile analytes from the soil matrix so they can be introduced into a gas chromatograph in the most concentrated form possible.

Current methods

Current methods for determining volatile organics in soil can be classified into the following groups:

1. Static or dynamic headspace analysis
2. Solvent extraction—direct injection
3. Solvent extraction—purge-and-trap analysis

In headspace analysis, the soil sample is placed in a closed container and the volatile components are allowed to partition among the gaseous phase, the solid soil surface, and the soil moisture. By the static method, once equilibration at a given temperature has occurred, an aliquot of the headspace is sampled and subjected to

GC analysis (Kiang and Grob 1986). Using the dynamic method, the vapors are continuously swept away and generally collected on a sorbent material. After a suitable time period the sorbent is either solvent-extracted or thermally desorbed (Amin and Narang 1985, Brazell and Maskarinec 1981, Murray and Riley 1973). Several investigators have developed methods based on the dynamic headspace method whereby the volatiles are stripped from a soil/water slurry using a conventional purge-and-trap instrument (Ramstad and Nestrick 1981, Wang et al. 1983).

Static headspace analysis suffers from a dependence on the constancy of the gaseous-to-condensed phase partition coefficients. Clearly these will differ from matrix to matrix, causing calibration difficulties. Thus this method is best suited to situations where quick qualitative information is sufficient. The dynamic method requires complete removal of the volatile, which can be rather slow. Attempts to increase the speed by increasing the equilibration temperature have not been completely successful (Brazell and Maskarinec 1981). Kolb and Pospisil (1977) have presented a multiple headspace analysis approach that does not require complete removal of the volatile or prior knowledge of the partition coefficient to calculate the total amount of analyte present, although it does suffer from matrix effects as does the single equilibration method. This method requires several analyses per sample, which is too time-consuming and costly for routine soil analysis. In our laboratory, however, Leggett (personal communication) tested this method, confirming its utility for both identification and quantitation of volatiles.

A second alternative is solvent extraction of the soil followed by direct injection of the extract for GC analysis. DeLeon et al. (1980) proposed using a hexadecane extraction solvent, which would not interfere with the chromatogram in the region where the volatiles elute. Henderson et al. (1981) recommended methanol in a similar method. The simplicity of this procedure is attractive, since a number of samples may be processed simultaneously and sequentially injected into a GC. It suffers, however, from the inability to concentrate the sample by solvent evaporation, leading to poor detectability since only a few microliters of solvent can be directly injected into a GC. The late elution of less volatile substances that would also be co-extracted would cause trouble for subsequent analyses, thereby requiring extensive column bakeout between injections and leading to very poor sample throughput.

Another approach is soil extraction using an organic solvent and subsequent addition of the extract to an aqueous matrix followed by purge-and-trap analysis. The major limitation of this method is the use of an extractant that is highly soluble in water. The advantages are the ability to process a number of samples simultaneously with subsequent analysis using a purge-and-trap analyzer. This technique has advantages over direct injection of the extract in two ways. First, larger sample volumes can be used, thereby lowering detection limits. In addition, less volatile contaminants are not purged efficiently, thereby reducing or eliminating problems associated with the late elution of less volatile contaminants.

Because of the advantage of this last approach and its ease of use with available instrumentation, this is the approach most often taken commercially for routine analy-

sis of volatiles in soil. A method involving use of tetraglyme as the extraction solvent was developed at Battelle (Warner et al. 1983, 1984; Gurka et al. 1984). Tetraglyme was chosen because it is miscible with water as well as with a wide range of organic solvents and, being nonvolatile, would not be purged from water during purge-and-trap analysis. A similar method utilizing methanol as the extraction solvent has been accepted as the solvent of choice by the EPA Office of Solid Waste SW846 (EPA 1982). Methanol is also miscible in water and, while it is quite volatile, it is not efficiently purged from water due to its high solubility. No direct comparison of the utility of using methanol or tetraglyme has been reported.

Objectives

There are four major objectives of this study:

1. To compare the efficiency of methanol and tetraglyme in extracting volatile organics from soil as well as their utility in subsequent analysis using the purge-and-trap method.

2. To define the desorption kinetics associated with both solvents to establish the equilibration periods necessary to approach complete extraction.

3. To document what losses might occur if proper subsampling procedures were not used during analysis.

4. To assess whether the presence of an oily residue in the soil affected either the choice of extraction solvent or the length of time necessary to achieve extraction.

To conduct these studies we chose to use three different soils that differed considerably in their physical and chemical properties; they were vapor-equilibrated with a set of volatile organics. This is in contrast to many other experiments where the volatiles were added to a suspension of soil in the extraction solvent. While our method suffers from a lack of knowledge of the total amount of analyte present, each organic substance is allowed to interact with the soil for at least a week before the extraction solvent is added. In this way we hope to simulate better the type of interaction that would occur in a real-world sample. This type of interaction probably does not occur when a suspension of soil in solvent is spiked.

The four volatiles chosen for study included two volatile aromatics, benzene and toluene, and two volatile halocarbons, chloroform and tetrachloroethylene. Benzene, toluene, and tetrachloroethylene are among the three volatile organics most often observed in contaminated soil. Chloroform was selected instead of trichloroethylene because of the background of trichloroethylene in our laboratory where it has been used for years as a refrigerant in the cold room facilities.

EXPERIMENTAL METHODS

Analytical instrumentation

All analyses discussed in this report were obtained from a Hewlett Packard 5992B Gas Chromatograph/Mass Spectrometer (GC/MS) equipped with a Hewlett Packard

Model 7675A Purge-and-Trap Sampler. The GC/MS was operated in the electron impact mode, and mass spectral data were obtained using selective ion monitoring. The primary ions chosen for quantitation and the secondary ions used for confirmation of analyte identity are given in Appendix A (Table A1).

A sample volume of 60 mL was sparged with helium at 60 mL/min for 10 min and the purged volatiles were collected on a Tenax collection tube. Subsequently, the collection tube was heated to 180°C for 5 min and the desorbed compounds were transferred to the head of a GC column maintained at 90°C. Desorbed compounds were separated on a 45 x 0.22 cm Porapak QS column, which was held for 2 min at 90°C and then temperature-programmed from 90° to 200°C at 10°/min with a helium carrier of 20 mL/min. Retention times for chloroform, benzene, deuterobenzene, tetrachloroethylene, and toluene are given in Appendix A (Table A1).

Chemicals

The methanol used in this study was Baker Analyzed HPLC grade and was used without further purification. The tetraethylene glycol dimethyl ether (tetraglyme) used was obtained from Aldrich Chemical Company and was reported to be 99% pure. Except as noted, it was also used without further purification. Water used in the purging chamber was obtained locally from a deep groundwater well. Extensive characterization had indicated this water was free from contamination with volatile organics.

Standard materials of chloroform, benzene, tetrachloroethylene, and toluene used to prepare analytical standards were obtained from the U.S. Environmental Protection Agency (EPA). They are supplied by EPA dissolved in methanol at a concentration of 10,000 µg/mL.

The chloroform, benzene, tetrachloroethylene, and toluene added to soils were Mallinckrodt Nanograde, Fisher Pesticide Residue, Eastman Reagent grade (stabilized with ethyl alcohol), and Mallinckrodt Analytical Reagent grade, respectively.

Tetradecane, used to simulate the presence of oil, was obtained from Aldrich Chemical Company. It was reported to be 99% pure. Deuterobenzene, used as the internal standard, was also obtained from Aldrich and listed as 100% pure.

Preparation of standards

A 100 mL volumetric flask was filled two-thirds full with methanol. Using a glass volumetric pipet, 1.00 mL each of the 10,000 µg/mL solutions of chloroform, benzene, tetrachloroethylene, and toluene obtained from the EPA were added and the flask was brought to volume with methanol. This combined stock standard had concentrations of each analyte of 100 µg/mL.

A set of five working standards was prepared by diluting 1.00 mL of the combined stock standard with methanol in volumetric flasks as shown in Appendix A (Table A2).

Linearity test

An experiment was conducted to determine if the GC/MS response was linear as a function of concentration for the four analytes of interest. The five working standards and stock standard described earlier were used for the test. A 50-µL volume of each standard was analyzed using the normal purge-and-trap procedure. The analytical range examined was from 50-5000 ng. The results for each analyte (Table A3) and a summary of the relative standard deviations (Table A4) are presented in Appendix A.

Using the criteria set forth in EPA Method 624 (EPA 1984a), the response is linear over the mass ranges examined. For chloroform, benzene, and toluene, the linear range was 50-5000 ng. For tetrachloroethylene, no response was obtained for the 50-ng standard, and thus the linear range was from 100-5000 ng.

Soils

Three different soils were used in this study. Soil 1 was USATHAMA Standard Soil, soil 2 an organic-rich soil from Point Barrow, Alaska, and soil 3 a sandy soil obtained near Lebanon, N.H. The percent organic carbon, clay content, pH, and cation exchange capacities of these soils are presented in Appendix A (Table A5). Organic carbon contents varied from less than 0.5% for soil 3 to 6.69% for soil 2 as determined by carbon, hydrogen, and nitrogen analysis. Clay contents varied from 11.3% for soil 3 to 53.6% for soil 1 as determined by standard hydrometer analysis.

Preparation of volatile-contaminated soil

Soils chosen for study were contaminated with the four volatile organics by vapor equilibration. The soils were air dried, ground with a mortar and pestle, and placed in a desiccator that contained 50 mL of a solution of equal masses of chloroform, benzene, toluene, and tetrachloroethylene. Soils were equilibrated for at least a week prior to use.

Table 1. Recovery of volatiles from successively weighed out subsamples of soil 2.

	Concentration found (µg/g)			
Subsample	*Chloroform*	*Benzene*	*Tetrachloroethylene*	*Toluene*
		Methanol		
2	2985	4644	6067	6334
4	2498	4030	6218	6448
6	2490	4066	6287	6348
8	2235	3731	6041	6174
10	1600	2735	5560	5512
		Tetraglyme		
1	3710	5373	5671	6429
3	2977	4784	6829	6990
5	2669	4156	5895	6305
7	2235	3725	6081	6215
9	1993	3351	6061	5957

A series of preliminary experiments indicated it was impossible to contaminate a bulk sample and weigh out replicate subsamples that contained a reproducible amount of volatile contaminant. Volatiles were lost quickly during the weighing process even when care was taken to expedite the weighing step as much as possible. This is demonstrated in Table 1, where successively weighed samples were extracted with methanol or tetraglyme and analyzed as usual. This problem was particularly troublesome for chloroform and benzene, probably due to a combination of high vapor pressures and lower sorption coefficients for these compounds.

To reduce the impact of this problem, the soil was thoroughly mixed and 2.0-g subsamples were weighed into individual glass scintillation vials. These vials were then exposed to the vapors of the four volatile organics by placing them in the desiccator and allowing exposure to the four volatiles for a week as usual.

Detection limit estimation

Estimates of the method detection limit were obtained by two different procedures. The first study was conducted according to the EPA protocol (EPA 1984a). In this procedure a series of matrix samples are spiked at one level and carried through the entire measurement process. The spike level chosen was the lowest standard tested in the linearity test that gave a response for all four analytes (100 ng). The method detection limit (MDL) according to the EPA protocol is defined as:

$$MDL = S_m (t_{.99})$$

where S_m is the standard deviation of responses and $t_{.99}$ is the Student's t value for a one-tailed test at the 99% confidence level (n-1 degrees of freedom). In this test, a 2-g sample of soil 1 in a methanol suspension was spiked and extracted with 20 mL of methanol. A 100-µL subsample was injected into the purge-and-trap analyzer. Concentrations on a soil basis corresponded to 10 µg/g for each analyte.

Seven replicates were carried through the measurement process; the results are presented in Table 2. Method detection limits on a soil basis ranged from 2.7 µg/g for benzene to 3.3 µg/g for tetrachloroethylene.

Reporting limits were also obtained using the protocol described in the USATHAMA Quality Assurance Manual (USATHAMA 1985). In this procedure, a target value is estimated, duplicate matrix spikes are made at 0, 0.5, 2, and 10 times that level, and samples are carried through the entire measurement process. Reporting limits are based on the method described by Hubaux and Vos (1970) as specified in USATHAMA (1985).

We actually made duplicate soil spikes at 0, 0.5, 1, 2, 5, 10, and 20 times the estimated levels. The results are presented in Table 3. Reporting limits obtained using this procedure ranged from 2.6 to 4.6 µg/g. Comparing the two methods, for chloroform the EPA procedure gave 2.7 µg/g and the USATHAMA method gave 2.6 µg/g. For benzene, the values were 2.7 vs 2.9 µg/g, for toluene 3.3 vs 3.5 µ/g, and for tetrachloroethylene 3.3 vs 4.5 µg/g. Considering the differences in the two protocols used, the results were very consistent.

Table 2. Results of detection limit test according to EPA protocol.

	Concentration (µg/g)			
Replicate	*Chloroform*	*Benzene*	*Toluene*	*Tetrachloro-ethylene*
1	8.48	12.19	14.39	11.59
2	7.07	10.72	12.01	9.49
3	7.10	10.55	12.40	8.79
4	8.98	12.32	13.88	11.24
5	8.73	12.45	14.04	11.12
6	9.19	12.50	14.37	11.19
7	8.69	12.34	14.00	10.88
$\bar{X}$	8.32	11.87	13.58	10.61
S_m	0.873	0.849	0.967	1.05
MDL*	2.7	2.7	3.0	3.3

* Assuming 1.00 mL of extract is added to the purging chamber. MDL = S_m ($t_{.99}$) where S m is the standard deviation, $t_{.99}$ is the Student's t value for a one-tailed test at the 99% confidence level, and MDL is the method detection limit.

Table 3. Results of reporting limit test according to USATHAMA protocol.

	Concentration (µg/g)			
Spike level (µg/g)	*Chloroform*	*Benzene*	*Tetrachloro-ethylene*	*Toluene*
0	< d†	< d	< d	< d
	< d	< d	< d	< d
0.5	< d	2.05	< d	2.47
	< d	1.32	< d	2.01
1.0	< d	2.18	< d	3.10
	< d	1.93	< d	2.94
2.0	1.27	3.71	< d	4.82
	1.71	3.78	< d	4.35
5.0	4.42	6.45	3.85	7.82
	5.33	6.36	3.27	7.82
10.0	9.78	13.82	11.51	15.77
	9.59	13.51	11.71	15.61
20.0	17.21	22.51	21.01	24.61
	18.02	22.58	22.49	25.79
RL_T	2.6	2.9	4.6*	3.5

* Value defaults to 5.0 since no standards below 5 µg/g standard were tested.
† No detectable response.

Soil extraction and analysis procedure

Soils used in this study were extracted as follows. A 20-mL aliquot of either methanol or tetraglyme was added to each scintillation vial containing the 2-g soil sample, the vials were capped, and the soil was dispersed for 1 min using a vortex mixer. The vials were then placed on a wrist-action shaker for the appropriate amount of time. For kinetic studies, the vials were shaken for time periods ranging from 1 min to 4 hr. For replicated studies, comparing methanol and tetraglyme, a 4-hr period was generally selected. In all cases the shaker was set to its highest speed and the vials were positioned at a 45° angle.

The vials were then centrifuged at 2000 r/min for 5 minutes to obtain a clear supernatant. An aliquot of this supernatant (volumes ranged from 50–200 µL) and a 5-µL aliquot of an internal standard solution (418 µg/mL) were then added to a purging chamber and analyzed as described in Analytical Instrumentation above.

RESULTS AND DISCUSSION

Purging efficiency

In a number of experiments, to be discussed later, the ability of methanol and tetraglyme to extract volatile organics from soil will be compared. To assure that any observed differences are due to differences in extraction efficiency and not a result of a retardation of stripping efficiency in the subsequent purging step due to the presence of either solvent, a study was conducted to compare the purging efficiencies of water-methanol and water-tetraglyme solutions. The ratio of organic solvent to water was 1:60 in both cases, somewhat lower than the 1:25 ratio recommended as a maximum elsewhere (Gurka et al. 1984, EPA 1982).

To investigate this question a series of 10 replicate standards were analyzed. In each case 50 µL of the 20 µg/mL standard (1.0 µg) was added to 60 mL of water in the purging chamber along with 5 µL of internal standard solution. To half of these determinations, a 1.00-mL aliquot of methanol was added as well; to the other half, 1.00 mL of tetraglyme was added. All samples were purged, and the concentrations of the four volatile organics were determined as usual. The results are presented in Table 4. For chloroform, benzene, and toluene, the mean recovery for standards containing methanol and tetraglyme were not significantly different at the 95% confidence level. For tetrachloroethylene, the mean recoveries were significantly different, although recovery for tetraglyme was only 8% lower than methanol. We used maximum ratios of 1:600 (100 µL of solvent in 60 mL of water) of organic solvent to water in subsequent tests in this study, so even the small effect observed for tetrachloroethylene at a 1:60 solvent-to-water ratio would be reduced or eliminated at the much higher dilutions. Therefore we feel that any differences observed in subsequent experiments comparing determinations using methanol or tetraglyme extracts are not due to differences in purging efficiency.

Table 4. Results of purging efficiency test.

	Mass found (μg)							
	Chloroform		*Benzene*		*Tetrachloro-ethylene*		*Toluene*	
Replicate	*MeOH**	*TG†*	*MeOH*	*TG*	*MeOH*	*TG*	*MeOH*	*TG*
1	0.954	0.945	0.969	0.936	0.966	0.921	0.976	0.916
2	1.019	0.969	1.034	0.952	1.015	0.917	1.041	0.924
3	0.974	1.048	0.976	1.056	1.008	0.989	1.003	1.065
4	1.095	1.017	1.096	1.017	1.122	0.983	1.114	0.991
5	1.029	0.948	1.031	0.932	1.100	0.980	1.048	0.932
$\overline{X}$	1.014	0.985	1.021	0.979	1.042	0.958	1.036	0.966
S	0.0548	0.0453	0.0515	0.0551	0.0660	0.0358	0.0523	0.0629
t	0.912		1.245		2.502**		1.914	

* MeOH—1.00 mL of methanol added to purging chamber.
† TG—1.00 mL of tetraglyme added to purging chamber.
** Means are significantly different at the 95% level ($t_{.05}$ = 2.306).

Determining background concentration of volatiles in methanol and tetraglyme

To determine the concentrations of chloroform, benzene, tetrachloroethylene, and toluene in methanol and tetraglyme, three replicate 1.00-mL aliquots from individual, freshly opened bottles of the two solvents were analyzed. These bottles were taken from the same lots used throughout the study. Determinations were conducted as usual using a deuterobenzene internal standard. The results are presented in Table 5.

For both solvents, concentrations of chloroform and tetrachloroethylene were below method detection limits, estimated at 26 and 40 ng/mL, respectively. For methanol, the concentration of benzene was also below a detection limit estimated at 28 ng/mL, while the level of benzene in tetraglyme was determined to be 34 ng/mL. Toluene was detected in both solvents with levels of 107 and 54 ng/mL for methanol and tetraglyme, respectively. While no attempt was made to determine levels of other volatiles, higher molecular weight aromatics such as the xylenes were clearly detectable in both solvents.

For soil analysis, the amount of solvent added to the stripping chamber is based on the total amount of volatiles present. For soils with very low concentrations, both the SW846 (EPA 1982) method and that from Gurka et al. (1984) recommend a maximum of 200 μL of solvent to 5 mL of water. Thus for toluene, as much as 21 ng would be present from the solvent if methanol were used and 11 ng for tetraglyme. Tetraglyme would also contain 7 ng of benzene. For soils with higher concentrations, less extraction solvent is added to the purging chamber, and the levels present in the solvent be-

Table 5. Determination of background concentrations of volatile in methanol and tetraglyme.

	Mean concentration (ng/mL)		
Volatile	*Methanol*	*TG**	*TG (rotovap)†*
Chloroform	< d**	< d	< d
Benzene	< d	34	< d
Tetrachloroethylene	< d	< d	< d
Toluene	107	54	< d

* Tetraglyme
† Tetraglyme after purified by rotary evaporation at 97° for 3½ hr.
** < d = concentrations lower than method detection limits of 12.4, 4.5, 32.5, and 3.3 ng/mL for chloroform, benzene, tetrachloroethylene, and toluene, respectively, calculated on a volumetric basis from results shown in Table 2.

came insignificant at the detection limits found here. However, for determination of benzene and toluene at low levels in fairly uncontaminated soil, the amount present in the solvent would increase the analytical uncertainty.

To determine if the volatiles present in tetraglyme could be easily removed, a 100-mL aliquot of tetraglyme was placed in a rotary evaporator and heated to 97°C under vacuum for 3½ hr (Gurka et al. 1984). Three replicate subsamples of this degassed tetraglyme were analyzed as above; the results are shown in Table 5. The levels of all four volatiles were below method detection limits. Thus, while commercial tetraglyme has measurable concentrations of aromatic hydrocarbons, these can be reduced to insignificant levels by simple rotary evaporation, using standard equipment available in most laboratories. Methanol, on the other hand, also contains detectable levels of toluene and higher molecular weight aromatics, but cannot easily be purified. Thus for determining very low concentrations (< 1 µg/g), tetraglyme seems the more desirable extraction solvent, although all solvent used for extraction would need to be degassed before use.

Extraction kinetics

In the next experiment we sought to determine the kinetics associated with extraction of volatiles using either methanol or tetraglyme. Shaking times of 1 min have been suggested by both Gurka et al. (1984) and the EPA (1982), although samples are allowed to stand for an indefinite amount of time to allow suspended material to settle before a subsample is taken for analysis. We were unable to locate any information supporting such a short equilibration time, and results obtained with less volatile organics in the soil indicated a much longer extraction time was necessary to obtain near complete extraction (Jenkins and Leggett 1985, Jenkins and Walsh 1987).

To determine the rate at which these volatiles were extracted, a 2-g subsample of each soil was dispersed with a vortex mixer and shaken for periods of 1, 10, 30, 60, and 240 min with 20 mL of either methanol or tetraglyme. After each time increment, the vials were removed from the shaker, centrifuged at 2000 r/min for 5 min, and a 1.00-mL portion was removed for analysis. The vials were then vortexed again and replaced on the shaker. This was done for each of the three test soils with and without additional contamination with tetradecane. Tetradecane was used to simulate the behavior of a soil contaminated with an oily residue. The results of these tests are presented in Appendix A (Table A6-A9). It should be emphasized that results for methanol should not be compared with those using tetraglyme here since there was no replication in these studies. That comparison will be discussed later in experiments where sufficient replication was used to enable us to address this point directly.

It is difficult to draw general conclusions from the results of the kinetic studies because no consistent pattern was evident in the data. For example, when methanol was used to extract soil 2, a fairly regular increase in concentration with shaking time was observed for tetrachloroethylene (Fig. 1). Values increase from 2804 µg/g for a 1-min shaking time to 3318 µg/g for a 240-min shaking time. Results for toluene parallel those for tetrachloroethylene. In the same samples, however, benzene shows a regular decline in concentration with shaking time (Fig. 2), going from 1277 to 1233 µg/g. Results for chloroform parallel those for benzene. The small losses observed for the two most volatile components could be due to losses of vapor each time the vials were opened to remove subsamples.

In some other samples, a less regular change in concentration as a function of shaking time is observed. On the average, though, concentrations obtained after only a 1-min shaking time with either methanol or tetraglyme averaged 90% of the highest values obtained over the 4-hr shaking period. Concentrations obtained after a 10-min shaking time averaged 95% of the highest values obtained, and extending the shaking period beyond 10 min did not, on the average, improve analyte recoveries. We therefore suggest that a 10-min shaking time is a more dependable procedure than the 1-min time recommended elsewhere. Occasionally, use of only a 1-min shaking time resulted in less than 70% recovery (soil 3, chloroform, extracted with tetraglyme).

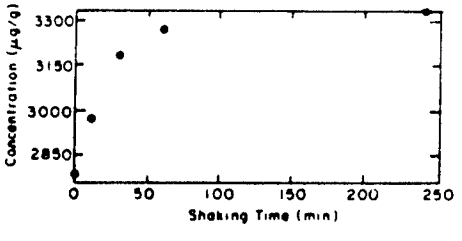

Figure 1. Results of kinetic study for benzene in soil 2.

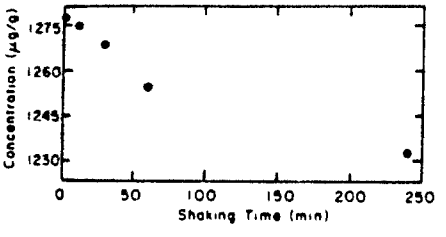

Figure 2. Results of kinetic study for tetrachloroethylene in soil 2.

However, results using the 10-min extraction period never underestimated the volatile concentration by more than 13% (soil 2, tetrachloroethylene, extracted with tetraglyme). There appeared to be no consistent difference between methanol and tetraglyme with respect to extraction kinetics.

The presence of an oily residue, as represented by those samples contaminated with tetradecane, did not appear to affect significantly the extraction kinetics. Visually it was evident that tetraglyme dissolved the tetradecane while methanol did not. It did not appear that lengthening the shaking time beyond 10 min was needed for oily soils.

Order of addition of sample and solvent

In Gurka et al. (1984) and EPA (1984), the procedures call for addition of soil to a premeasured volume of extraction solvent. In practice, however, we have observed commercial laboratories weighing out subsamples of soil into empty vials, followed by addition of the extraction solvent. Since we have observed rapid loss of volatiles from soil during some initial experiments, we suspected the latter procedure might result in lower determined concentrations due to volatilization losses.

To resolve this question we processed five replicates of soil 1 by each of two procedures. In the first procedure, 20 mL of tetraglyme was added to each glass scintillation vial and vapor-contaminated soil was added directly to the solvent as described in Gurka et al. (1984) and EPA (1982). The second method involved transferring the soil to an empty, capped vial, allowing it to stand 1 min and then adding 20 mL of tetraglyme.

The results of the test are presented in Table 6. For chloroform and benzene, there was a significant difference between the concentrations determined by the two procedures at the 95% confidence level. This amounted to a 16.0% higher mean value for chloroform and 10.4% higher mean value for benzene for those samples in which the soil was added directly to the solvent. Mean concentrations for tetrachloroethylene and toluene were not significantly different using the two procedures at the 95% confidence level.

Thus addition of the soil to the solvent made a measurable difference in determined concentrations for the two most volatile compounds. This was true even though the soil was allowed to stand for only 1 min in a closed vial before solvent was added. In practice, if a number of soils were weighed out before solvent was added, low recovery of the most volatile compounds would result, even if the vial were capped until the extracting solvent was added.

Comparison of methanol and tetraglyme extractants

In the final set of experiments, replicate 2-g subsamples of each of the three vapor-contaminated soils were extracted with either methanol or tetraglyme to compare directly the solvent's ability to extract volatiles from soil. The three different soils were tested on separate days, with and without an addition of tetradecane to simulate the presence of oil. Five replicates of each soil were extracted with either methanol or

Table 6. Comparison of order of addition: soil to solvent (method 1) or solvent to soil (method 2) using soil 1 extracted with tetraglyme.

	Concentration found (μg/g)							
	Chloroform		*Benzene*		*Tetrachloroethylene*		*Toluene*	
Replicate	*Method 1*	*Method 2*	*Method 1*	*Method 2*	*Method 1*	*Method 2*	*Method 1*	*Method 2*
1	5484	5301	7685	7875	10985	9957	12044	10512
2	6252	5484	8818	7686	11490	10985	12065	12045
3	6047	5023	8277	7475	10285	10437	10686	10947
4	6024	5377	8381	7702	11119	10735	11701	11116
5	6506	4936	8766	7254	10682	10498	11116	11329
$\bar{X}$	6063	5224	8385	7598	10912	10522	11522	11190
S	377	235	457	239	455	383	605	564
t	4.223*		3.412*		1.466		0.898	

* Significant at 95% confidence level ($t_{.95}$ for 8 df [degrees of freedom] = 2.306)

tetraglyme for 2 hr and the extracts were analyzed as usual. The soil was added directly to the solvent as described in Gurka et al. (1984).

All comparisons between methanol and tetraglyme extracts are taken from replicate determinations obtained on the same day, analyzed in random order. The results of individual determinations for soils not contaminated with tetradecane are presented in Appendix A (Table A10). A summary of the mean and standard deviation of each set of replicates is summarized in Table 7 along with the RSD and the calculated Student's *t* statistic comparing the mean values obtained for methanol vs tetraglyme extracts for each analyte on each soil. For soil 1, no significant differences were obtained for any of the four analytes at the 95% confidence level. The inability to detect a significant difference between the two extraction solvents was not a result of poor agreement among replicates. In fact, RSD values as low as 1.2% were detected for toluene extracted with methanol. Thus for soil 1, extraction with methanol and tetraglyme gave equivalent results.

For soil 3, a similar result was obtained. No significant differences between extraction solvents were found for any of the four analytes at the 95% confidence level. RSD values were somewhat higher for this soil, however—a result of the lower amount of volatiles present. While the ability to detect differences between the two solvents is therefore not as good, mean values obtained differed by less than 4.2% in all cases.

A somewhat different result was obtained for soil 2 (Table 7). For this soil, a significant difference between the mean values for the two extraction solvents was obtained for all four analytes. In all cases methanol was superior, with mean values differing by as much as 28.4% for chloroform to as little as 8.7% for toluene. As noted earlier, soil 2 had the highest organic carbon content (6.69% compared with 1.45 and < 0.5 for soils 1 and 3). Since adsorption of organic contaminants is thought to occur largely on natural organic matter, it appears that methanol is better at extracting volatiles from these sites. Thus, for soil 2, methanol extracts significantly higher amounts of all four analytes, with the order of difference being chloroform > benzene > tetrachloroethylene > toluene.

Table 7. Summary of results comparing extraction efficiency of methanol and tetraglyme.

	Summary statistics (μg/g)						
	Methanol			*Tetraglyme*			
Soil	$\bar{X}$	S	RSD	$\bar{X}$	S	RSD	t
			Chloroform				
1	5051	351	6.9%	4862	460	9.5%	0.73
2	2420	189	7.8%	1733	238	13.7%	5.06*
3	528	133	25.2%	545	132	24.2%	0.20
			Benzene				
1	5948	295	5.0%	5674	271	4.8%	1.53
2	3289	244	7.4%	2545	309	12.1%	4.23*
3	1066	186	17.4%	1079	165	15.3%	0.12
			Tetrachloroethylene				
1	4535	65	1.4%	4459	106	2.4%	1.37
2	4772	142	3.0%	4219	233	5.5%	4.53*
3	2291	144	6.3%	2389	107	4.5%	1.22
			Toluene				
1	4760	58	1.2%	4624	148	3.2%	1.92
2	4993	128	2.6%	4559	224	4.9%	3.76*
3	2107	150	7.1%	2177	90	4.1%	0.89

* *t* values in excess of 2.31 are statistically significant at the 95% confidence level.

Comparison of methanol and tetraglyme on soils containing oily residue

One of the major advantages claimed for tetraglyme as an extractant is its ability to dissolve any oily residue present in the soil, thereby capturing any volatile organics present. This is not the case for methanol, which is not miscible with long-chain aliphatic hydrocarbons, often the type of compounds prevalent in oily matrices.

To see if the presence of such a residue affected the extraction efficiency of methanol compared to tetraglyme, we first vapor-contaminated soil replicates with the four volatiles as usual and then added tetradecane. After a short equilibration period, the soils were extracted with either methanol or tetraglyme and the concentrations of the four volatiles were determined as usual. Data for individual replicates of each soil are presented in Appendix A (Table A11). The mean, standard deviation, relative standard deviation, and Student's *t* statistic for each volatile in all three soils are summarized in Table 8.

For soil 3, no significant differences were found for any of the four volatiles, a result identical to that observed for this soil without the presence of tetradecane.

Table 8. Summary of results comparing extraction efficiency of methanol and tetraglyme for soils contaminated with an oily residue of tetradecane.

	Summary statistics (μg/g)						
	Methanol			*Tetraglyme*			
Soil	$\bar{X}$	S	RSD	$\bar{X}$	S	RSD	t
				Chloroform			
1	7440	143	1.9%	7128	180	2.5%	3.04*
2	4896	73	1.5%	4284	216	5.0%	6.01*
3	2101	93	4.4%	2036	98	4.8%	1.08
				Benzene			
1	9761	59	0.6%	9523	96	1.0%	4.73*
2	5574	43	0.8%	5180	142	2.7%	5.95*
3	2496	86	3.5%	2456	124	5.0%	0.59
				Tetrachloroethylene			
1	9307	122	1.3%	9329	374	4.0%	0.12
2	5153	114	2.2%	5199	74	1.4%	0.76
3	2097	95	4.4%	2132	95	4.5%	0.59
				Toluene			
1	9282	83	0.9%	9125	262	2.9%	1.28
2	5141	128	2.5%	4986	50	1.0%	2.52*
3	2148	90	4.2%	2151	89	4.1%	0.05

* *t* values in excess of 2.31 are statistically significant at the 95% confidence level.

For soil 2, a significant difference was observed for chloroform, benzene, and toluene, but not for tetrachloroethylene. In all cases where a difference was found, methanol was found to be superior: 10.8% higher for chloroform, 7.1% for benzene, and 3.0% for toluene. These values are somewhat lower than observed for soil 2 without the presence of tetradecane, but methanol was nevertheless superior.

The results for soil 1 differed from those observed without the presence of tetradecane. For chloroform and benzene, significantly higher results were obtained using methanol (Table 8). For tetrachloroethylene and toluene, no significant difference was observed. The difference for chloroform and benzene amounted to 4.2% and 2.5%, respectively.

Overall, even with the presence of tetradecane, methanol performed as well or better than tetraglyme. The consistently better performance with soil 2 is interesting and likely a result of the higher organic carbon content of this soil. This difference may be due to the smaller size of the methanol molecule compared to tetraglyme, which allows it to penetrate small pores to a greater extent than tetraglyme. The much lower viscosity of methanol probably plays a role as well.

CONCLUSIONS AND RECOMMENDATIONS

Kinetic studies indicate that extraction of volatile organics by either methanol or tetraglyme is rapid. On the average over 90% is extracted in the first minute. A 10-min extraction period is recommended.

In replicated trials, methanol was found to be as good or better than tetraglyme in recovering four volatiles from three vapor-contaminated soils. In the most extreme case, methanol was found to extract 28.4% higher amounts of chloroform from a soil rich in natural organic matter. Even in soils contaminated with an oily residue, methanol achieved better analyte recovery even though it was not as successful as tetraglyme in dissolving the oil.

Methanol also seems to be the more desirable solvent from a practical point of view. Unlike tetraglyme, methanol does not foam during purge-and-trap analysis, so a higher methanol-to-water ratio is tolerable. Tetraglyme, like other ethers, is also susceptible to formation of peroxides, which can be dangerous. Methanol is much less viscous than tetraglyme, which makes it much easier to handle with pipets and syringes. In the long run, this will lead to better overall analytical precision.

The only major advantage we observed for tetraglyme was the ability to purify it using a rotary evaporator. Therefore for very low level analysis of aromatics, tetraglyme may be the preferred solvent.

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APPENDIX A: EXPERIMENTAL DATA

Table A1. Gas chromatographic retention times and GC/MS ions monitored for analytes and internal standard.

Compound	GC retention time* (min)	Ions monitored (m/Z) Primary	Confirmatory
Chloroform	5.4	83	85
Deutercbenzene†	6.3	84	56
Benzene	6.4	78	77
Tetrachloroethylene	8.3	166	164
Toluene	8.8	91	92

*For 45 cm Porapak Q5 column operated under the following conditions: helium flow rate 20 mL/min, column temperature held at 90°C for 2 min, and programmed from 90° to 200°C at 10°/min.

†Used as an internal standard.

Table A2. Preparation of working standards from combined analyte stock standard.

Standard	Volume of combined std.* (mL)	Dilution volume (mL)	Concentration of each analyte (µg/mL)
A	1.00	5	20
B	1.00	10	10
C	1.00	25	4.0
D	1.00	50	2.0
E	1.00	100	1.0

*Combined analyte stock standard had analyte concentrations of 100 µg/mL.

Table A3. Linearity test data.

Standard	Mass present (ng)	Normalized area (area units)	Response factor (area units/ng)
		Benzene	
Stock	5000	2.2100	4.42×10^{-4}
A	1000	0.4409	4.41×10^{-4}
B	500	0.2270	4.54×10^{-4}
C	200	0.0923	4.61×10^{-4}
D	100	0.0502	5.02×10^{-4}
E	50	0.0279	5.57×10^{-4}
		Chloroform	
Stock	5000	1.3673	2.73×10^{-4}
A	1000	0.2626	2.63×10^{-4}
B	500	0.1277	2.55×10^{-4}
C	200	0.0520	2.60×10^{-4}
D	100	0.0268	2.68×10^{-4}
E	50	0.0137	2.74×10^{-4}
		Toluene	
Stock	5000	2.6764	5.35×10^{-4}
A	1000	0.5729	5.73×10^{-4}
B	500	0.2901	5.80×10^{-4}
C	200	0.1140	5.70×10^{-4}
D	100	0.0502	5.02×10^{-4}
E	50	0.0294	5.88×10^{-4}
		Tetrachloroethylene	
Stock	5000	0.36162	7.23×10^{-5}
A	1000	0.08125	8.12×10^{-5}
B	500	0.03694	7.39×10^{-5}
C	200	0.01291	6.46×10^{-5}
D	100	0.0047	4.70×10^{-5}
E	50	---	---

Table A4. Results of linearity test.

Analyte	Mean response factor (normalized area/ng)	Relative standard deviation (%)
Chloroform	2.66×10^{-4}	2.83
Benzene	4.76×10^{-4}	9.54
Tetrachloroethylene	6.78×10^{-5}	19.2
Toluene	5.58×10^{-4}	5.90

Table A5. Characteristics of soils used in this study.

Soil	Organic carbon (%)	Clay (%)	pH	Cation exchange capacity (milliequiv./100 g)
1	1.45	53.6	6.2	9.7
2	6.69	20.1	---	---
3	< 0.5	11.3	---	---

Table A6. Results of study to determine rates of extraction with methanol.

Extraction time (min)	Concentration (µg/g) Chloroform	Benzene	Tetrachloro-ethylene	Toluene
		Soil 1		
1	124	419	1716	1840
10	117	410	1677	1861
30	118	407	1647	1829
60	118	411	1723	1844
240	120	412	1669	1821
		Soil 2		
1	603	1277	2804	3315
10	595	1276	2979	3502
30	586	1270	3171	3602
60	576	1255	3275	3701
240	574	1233	3318	3769
		Soil 3		
1	5.38	15.8	326	253
10	5.38	16.9	327	246
30	5.66	17.3	347	250
60	5.65	17.2	344	244
240	6.10	17.7	371	254

Table A7. Results of study to determine rates of extraction with tetraglyme.

Extraction time (min)	Concentration (µg/g) Chloroform	Benzene	Tetrachloro-ethylene	Toluene
		Soil 1		
1	505	1316	2032	2565
10	541	1396	1964	2522
30	513	1352	2052	2553
60	540	1368	1974	2476
240	541	1377	1976	2496
		Soil 2		
1	849	1733	2886	3529
10	914	1863	3011	3662
30	926	1892	3124	3775
60	956	1940	3239	3861
240	946	1943	3471	4095
		Soil 3		
1	3.28	10.4	247	180
10	4.36	12.1	278	189
30	3.95	12.7	273	189
60	4.52	12.8	269	187
240	4.87	13.5	280	189

Table A8. Results of study to determine rates of extraction with methanol for soils contaminated with tetradecane.

Extraction time (min)	Concentration (µg/g) Chloroform	Benzene	Tetrachloro-ethylene	Toluene
		Soil 1		
1	162	532	1166	1763
10	165	538	1232	1735
30	165	543	1213	1606
60	166	539	1253	1609
240	198	626	1324	1694
		Soil 2		
1	202	484	3749	3097
10	207	493	3574	2934
30	214	499	3435	2863
60	215	506	3331	2789
240	209	490	3214	2646
		Soil 3		
1	< d*	12.2	348	249
10	< d	14.3	397	277
30	< d	13.4	358	246
60	< d	13.9	363	247
240	< d	14.7	381	267

* < d - concentration less than method reporting limit.

Table A9. Results of study to determine rates of extraction with tetraglyme for soils contaminated with tetradecane.

Extraction time (min)	Concentration (μg/g) Chloroform	Benzene	Tetrachloro-ethylene	Toluene
		Soil 1		
1	215	680	1268	2054
10	205	667	1267	1873
30	207	668	1324	1856
60	206	676	1316	1737
240	207	672	1351	1742
		Soil 2		
1	289	685	4276	3574
10	293	698	4115	3431
30	298	704	3873	3266
60	297	700	3665	3094
240	308	719	3790	3181
		Soil 3		
1	4.70	35.6	598	444
10	4.85	37.9	626	455
30	—	--	--	--
60	4.13	37.4	604	439
240	5.95	43.2	672	501

Table A10. Comparison of extraction efficiency: methanol (MeOH) vs tetraglyme (TG).

	Concentration found (µg/g)							
	Chloroform		Benzene		Tetrachloroethylene		Toluene	
Replicate	MeOH	TG	MeOH	TG	MeOH	TG	MeOH	TG
				Soil 1				
1	5541	5324	6338	5990	4459	4552	4707	4740
2	5183	5141	6050	5841	4592	4503	4808	4716
3	5073	4969	6004	5714	4612	4450	4837	4626
4	4845	4739	5801	5533	4497	4510	4732	4664
5	4611	4135	5547	5293	4513	4281	4717	4372
$\bar{X}$	5051	4862	5948	5674	4535	4459	4760	4624
S	351	460	295	271	65	106	58	148
t*	0.730		1.529		1.367		1.917	
				Soil 2				
1	2541	1703	3442	2458	4828	3988	4997	4279
2	2669	2088	3584	3003	4921	4575	5151	4878
3	2338	1811	3228	2636	4709	4322	4938	4659
4	2372	1613	3251	2374	4846	4115	5068	4475
5	2182	1450	2940	2204	4557	4093	4813	4504
$\bar{X}$	2420	1733	3289	2545	4772	4219	4993	4559
S	189	238	244	309	142	233	128	224
t	5.055†		4.225†		4.532†		3.762†	
				Soil 3				
1	439	717	905	1290	2146	2377	1949	2245
2	760	654	1387	1222	2498	2396	2340	2197
3	458	482	994	985	2166	2319	2008	2108
4	466	459	1011	979	2297	2287	2097	2062
5	515	414	1034	921	2349	2564	2141	2273
$\bar{X}$	528	545	1066	1079	2291	2389	2107	2177
S	133	132	186	165	144	107	150	90
t*	0.203		0.117		1.220		0.894	

*Value for 8 df = 2.306 ($t_{.95}$).
†Significant at 95% confidence level ($t_{.95}$ for 8 df = 2.306)

Table A11. Comparison of extraction efficiency: methanol (MeOH) vs tetraglyme (TG). Soil contaminated with tetradecane.

	Concentration found (µg/g)							
	Chloroform		Benzene		Tetrachloroethylene		Toluene	
Replicate	MeOH	TG	MeOH	TG	MeOH	TG	MeOH	TG
				Soil 1				
1	7493	7157	9805	9677	9323	9545	9251	9288
2	7303	7368	9693	9449	9287	8673	9199	8674
3	7417	7071	9762	9477	9283	9391	9223	9156
4	7659	7170	9833	9556	9152	9459	9338	9183
5	7330	6872	9714	9457	9491	9576	9397	9324
$\bar{X}$	7440	7128	9761	9523	9307	9329	9282	9125
S	143	180	59	96	122	374	83	262
t	3.036*		4.729*		0.123		1.275	
				Soil 2				
1	4966	4626	5615	5426	5230	5185	5227	5052
2	4891	4292	5582	5128	5157	5143	5193	4965
3	4954	4297	5615	5152	5287	5220	5243	4980
4	4783	4138	5522	5135	4996	5315	4930	5013
5	4888	4066	5538	5060	5093	5132	5110	4920
$\bar{X}$	4896	4284	5574	5180	5153	5199	5141	4986
S	73	216	43	142	114	74	128	50
t	6.013*		5.945*		0.757		2.516*	
				Soil 3				
1	1990	2200	2356	2659	1989	2169	2032	2205
2	2046	1955	2516	2464	2148	2215	2200	2210
3	2233	2009	2563	2325	2003	2049	2069	2080
4	2140	1970	2567	2418	2178	2213	2218	2227
5	2096	2047	2479	2416	2166	2012	2219	2032
X	2101	2036	2496	2456	2097	2132	2148	2151
S	93	98	86	124	93	95	90	89
t†	1.076		0.592		0.589		.053	

*Significant at 95% confidence level ($t_{.95}$ for 8 df = 2.306).
†Critical t value for 8 df = 2.306 ($t_{.95}$).

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