

ANALYTICAL METHODS FOR THE DETERMINATION OF CARBON TETRACHLORIDE IN SOILS

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ABSTRACT

Improved methods for the determination of carbon tetrachloride are described. These methods incorporate purge-and-trap concentration of heated dry samples, an improved methanol extraction procedure, and headspace sampling. The methods minimize sample pretreatment, accomplish solvent substitution, and save time. The methanol extraction and headspace sampling procedures improved the method detection limits and yielded better sensitivity, good recoveries, and good performance. Optimization parameters are shown. Results obtained with these techniques are compared for soil samples from contaminated sites.

INTRODUCTION

Techniques and methods for chemical characterization and monitoring are essential for use in control programs to minimize health hazards. Research and development efforts can translate into new technologies for the detection of organic pollutants and into improvements in environmental cleanup. The success of these efforts is measured in reduced unit cost (with fewer steps in an analysis), decreased time required to report results to the user, and improved quality of the information provided. Desired characteristics of any new method are reduced turnaround time (faster), decreased cost of characterization (cheaper), improved achievement of desired data quality objectives (better), minimized generation of secondary waste through reduction of scale and elimination of steps, closer approximation to real-time analysis, and speedier site characterization.

The current methodology for determining volatile organic compounds (VOCs) in soil samples has demonstrated difficulties. Since its development, purge-and-trap analysis has been used to determine VOCs in aqueous matrices (EPA 1982, 1988a,b). Voice and Kolb (1993) showed that purge-and-trap analysis of soils may not meet the normal quality objectives for environmental data, because recoveries of organic compounds are low. Bianchi and coworkers (Bianchi and Varney 1989; Bianchi et al. 1991) suggested that purge-and-trap method recoveries could be improved by using elevated temperatures and longer purge times.

Methanol extraction procedures have been used successfully to analyze VOCs. Methanol is a highly favorable partitioning solvent and preservative, and it allows the researcher to perform multiple analyses and dilutions from a single sample. One disadvantage of methanol extraction at a 1:1 soil:methanol ratio is a loss in sensitivity at low concentrations because of elevated method detection limits.

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Headspace sampling has been used successfully for screening. The difficulty of using headspace methods for soil samples is that these methods rely on equilibrium partitioning of the analyte between the soil sample and the gas phase in a vial. As a consequence, the amount of a VOC sampled depends on the partition coefficient of the gas-soil matrix. Kolb et al. (1992) reported that equilibrium partitioning to the gas phase occurred when two soil samples were heated at 95°C, suggesting a possible way to overcome the matrix dependency in headspace sampling for the analysis of soils.

The focus of the present work was to develop an improved methodology for analysis of VOCs in any type of contaminated soil by building on the latest approaches of Kolb et al. (1992) and Bianchi and coworkers (Bianchi and Varney 1989; Bianchi et al. 1991). The data are compared with results obtained with standard U.S. Environmental Protection Agency (EPA) methodology. Soil samples from sites contaminated with carbon tetrachloride were used to validate the methodology and to determine accuracy, precision, and efficiency. Methods evaluated are summarized in Table 1.

EXPERIMENTAL DESIGN

Instrumentation

The gas chromatograph-mass spectrometer (GC-MS) used for sample analysis in this work was an HP-6890 gas system with an HP-5972 mass-selective detector (Hewlett-Packard, Wilmington, Delaware). Also used was an HP-5890 gas chromatograph Series II with electron capture detector (ECD). Instrument operating conditions are summarized in Table 2. Samples were introduced by an HP purge-and-trap concentrator with an autosampler and sampler heater or by an HP-7694 headspace sampler. In both instruments, heated lines were used to interface the concentrator or sampler unit to the gas chromatograph. No injector was used.

Reagents

Standard solutions containing VOCs were obtained from Protocol Analytical Supply, Inc. (Middlesex, New Jersey). These solutions meet or exceed all requirements and guidelines set forth in 40 *Code of Federal Regulations* Part 136. The stock solution was stored at 4°C, and dilutions

TABLE 1 Methods Evaluated

Sample Type	Preparation	Analyzer
Dry sample	Purge-and-trap concentrator, unheated or heated	GC-MS
Dry sample	Headspace sampling with autoanalyzer, heated	GC-ECD
Methanol extract	Purge-and-trap concentrator	GC-MS

TABLE 2 Instrument Conditions

Purge-and-Trap Sampler	
Sample temperature	25°C
Trap	Tenax-silica gel-charcoal
Purge time	11 min
Desorption temperature	225°C
Desorption time	4 min
Line temperature	100°C
Headspace Sampler	
Thermostating temperature	90°C
Thermostating time	30 min
Injection pressure	10 psi
Injection time	1.0 min
Transfer line temperature	110°C
Sample loop temperature	100°C
Sample loop	250 µL
Gas Chromatograph 1	
Column	0.31-mm × 30-m DB-624 ^a
Carrier flow gas	1 mL/min (He)
Oven profile	35°C (6 min) to 200°C (2.5 min) at 10°C/min
Detector	Mass spectrometer
Gas Chromatograph 2	
Column	0.53-mm × 105-m Restek-624 ^b
Carrier flow gas	12 mL/min (He)
Oven profile	90°C isothermal
Detector	Electron capture detector
Detector temperature	300°C
Make-up gas	68 mL/min (Ar with 5% methane)

^a Supelco (Bellefonte, Pennsylvania).

^b Restek (Bellefonte, Pennsylvania).

were prepared daily as needed. A new stock solution was prepared weekly. All standard solutions and dilutions were made by using purge-and-trap-grade methanol or ultra-resi-analyzed methanol from J.T. Baker (Phillipsburg, New Jersey).

Samples

Organic-rich soil samples were collected from the upper soil horizons at contaminated sites in Nebraska and Kansas. Samples were taken from several locations near known sources of contamination. Immediately after collection, samples were placed in coolers with dry ice (at least -78.5°C) and shipped to the laboratory. Samples were then placed in a freezer at -80°C . For methanol extraction, sample plugs weighing about 20-25 g were placed in vials, and 20-25 mL of methanol was added to give approximately a 1:1 ratio of methanol:soil.

RESULTS AND DISCUSSION

The detection of carbon tetrachloride at very low concentrations in soils has proven to be a challenge. Several methods have been reported for the analysis of high levels of VOCs in soils. However, all of the methods presented for the determination of low levels, in the parts-per-billion range, have deficiencies with loss of sample and sample detectability. Reliable methods for detecting VOCs at concentrations below the parts-per-billion threshold would be very useful for characterization and development of environmental programs.

Purge-and-Trap Concentration

Dry soil samples (heated or unheated) were subjected to purge-and-trap concentration and GC-MS analysis. The unheated dry samples (approximately 5 g) were placed in sample vials and purged with helium for 11 min. As the helium gas carries some of the VOCs into the trap, more carbon tetrachloride is expected to be released into the gas phase to maintain the equilibrium. Fluorobenzene, 1,2-dichlorobenzene- d_4 , and 4-bromofluorobenzene were used as surrogate spikes and internal standards to monitor the performance of the method. In all cases, recovery was below 60%, and only one sample showed carbon tetrachloride as a contaminant. Results are in Table 3.

A second set of subsamples was maintained at 90°C for 11 min by sampler heaters around the vials, while a flow of helium purged the VOCs and carried them to the trap for concentration. Results are also shown in Table 3. Recoveries were 82-110% for the surrogate spikes, and concentrations of carbon tetrachloride were higher than values obtained without heaters. These results were compared with the data obtained by headspace sampling and by standard methanol extraction with purge-and-trap concentration. The results for purge-and-trap concentration of heated dry samples are similar to those obtained with headspace sampling.

Methanol Extraction with Purge-and-Trap Concentration

The methanol extraction procedure was similar to the EPA method for middle and high values. The EPA method was modified to increase the amount of methanol introduced into the

TABLE 3 Concentrations of Carbon Tetrachloride ($\mu\text{g}/\text{kg}$) Obtained by Different Analytical Procedures

Sample	Purge-and-Trap Concentration of Dry Sample ^a		Methanol Extraction ^b	Heated Headspace Sampling ^c
	Unheated	Heated		
S-1	ND ^d	6.4	ND	9
S-2	2.5	52	ND	40
S-3	ND	2.3	ND	6
S-4	ND	ND	ND	ND

^a Analysis by GC-MS.

^b Standard Method 5030B, SW-846 Methodology.

^c Analysis by GC-ECD.

^d ND, not detected.

sample cell and to minimize detection limits. For these experiments, methanol was increased to a maximum ratio of 8:10 (8 mL of methanol + 2 mL of water for a final volume of 10 mL). The results showed a decrease in signal intensity, an increase in retention time, and a decrease in the resolution of the signals as the amount of methanol increased. Volumes of methanol below 5 mL were optimal for the analysis and detection of carbon tetrachloride in soil samples. For methanol:water ratios of 1:10, the method detection limits were reported as 10 $\mu\text{g}/\text{kg}$. Results are shown in Table 4.

Headspace Sampling

Headspace sampling has been proposed as an option for the analysis of soil samples. The main problem with this procedure is that the results depend on the partition coefficient between the soil sample and the gas phase. Whether phase equilibrium is actually established is unclear at this point. Mass-transfer limitations might hinder desorption of strongly adsorbing analytes from soils. To understand the behavior of soils in headspace sampling for the analysis of carbon tetrachloride, optimization studies were performed.

The effect of headspace equilibrium temperature on the normalized carbon tetrachloride signal is shown in Figure 1. Samples containing a standard solution of carbon tetrachloride (5 $\mu\text{g}/\text{L}$) in water were analyzed in duplicate. As Figure 1 shows, the signal increased as the

TABLE 4 Results for Determination of Carbon Tetrachloride ($\mu\text{g}/\text{kg}$) in Soils

Sample	Purge-and-Trap Concentration of Dry, Heated Sample ^a	Methanol Extraction ^a	Headspace Sampling ^b
S-5	ND ^c	29	31
S-6	ND	9J ^d	3
S-7	ND	7.6J	4.4
S-8	ND	ND	2.6
S-9	ND	ND	0.6
S-10	ND	ND	0.03

^a Analysis by GC-MS.

^b Analysis by GC-ECD.

^c ND, not detected.

^d Qualifier J indicates that value was estimated.

equilibration temperature increased up to a maximum at 90°C. Above 90°C, a decrease in signal was observed. This decrease was due to an increase in the concentration of water vapor, which interferes with the operation of the ECD.

The amount of sample introduced into the GC for analyses is related to the sample loop used. Sample loops ranging from 200 μL to 3 mL were used to optimize the headspace sampler. The loop size is not directly proportional to the magnitude of the signal, but the optimal size introduces a representative amount of the gas phase into the separation column and detector without adverse effects. This optimal loop size was found to be 250 μL . Larger sample loops allowed a large amount of water vapor to enter the column, decreasing the performance of the ECD.

A study of the effect of equilibration time on headspace sampling of soils (Figure 2) showed that time is one of the most important factors in the analysis of carbon tetrachloride. At shorter equilibration times, the sample does not reach equilibrium, and partitioning between the solid phase and the gas phase remains incomplete. With longer equilibration times, equilibrium can be reached; maintaining the equilibrium temperature makes results reproducible.

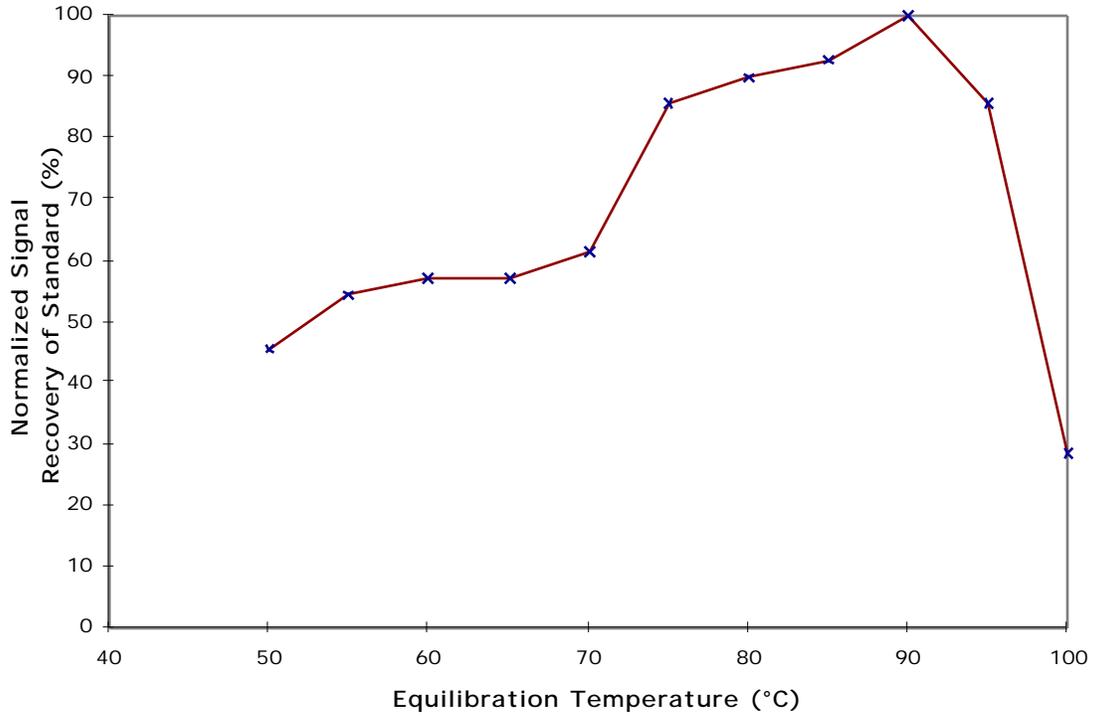


FIGURE 1 Effect of Temperature on the Carbon Tetrachloride Signal Obtained by Headspace Sample Introduction

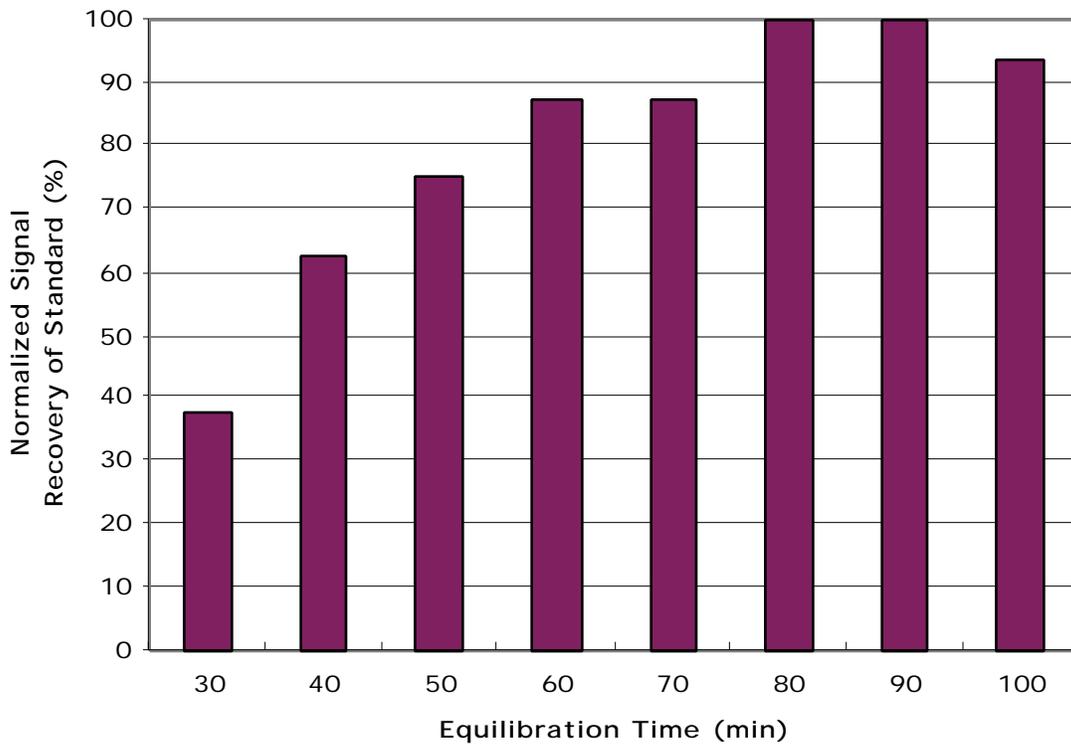


FIGURE 2 Effect of Equilibration Time on the Carbon Tetrachloride Signal

Results for Environmental Samples

Soil samples were collected from areas contaminated with low concentrations of carbon tetrachloride. The samples were analyzed by using the methods shown in Table 1. Results are in Table 4. Analysis with headspace sampling yielded concentrations similar to those obtained with the methanol extraction procedure. In addition, the combination of the sample introduction technique and the more sensitive detector (ECD) for chlorinated compounds decreased method detection limits compared to the other two techniques, typically to parts per trillion. Internal standard (1,1,2,2-tetrachloroethane) recoveries typically were 80-120%. Calibration plots were linear over two orders of magnitude.

Performance of the other two procedures under study was less satisfactory (Table 4). Results for samples prepared by methanol extraction had to be reported as estimates because of the high method detection limit. In addition, purge-and-trap concentration of dry, heated samples resulted in failure to detect the analyte in any sample; this lack of sensitivity makes this the least useful of the three procedures under study.

CONCLUSIONS

Methods for the determination of low concentrations of VOCs in soils are needed to speed site characterization. Three methods tested here were dynamic purge-and-trap concentration of heated dry samples, methanol extraction, and headspace sampling by static pressure. The traditional dry-heated purge-and-trap concentration method was shown to have low sensitivity for the analysis of carbon tetrachloride. Improvements in the methanol extraction procedure reduced the detection limit 20-fold from that reported for the EPA standard methodology; results were comparable with those for headspace sampling, which was shown to be a good alternative for the analysis of carbon tetrachloride in soil. Headspace sampling had good sensitivity for the detection of VOCs, good recoveries of internal standard and surrogate compounds, good performance, and minimal waste and time because of decreased sample preparation steps. In addition, the efficiency of headspace sampling, in terms of the numbers of samples per unit time, was about twice that of methanol extraction with purge-and-trap concentration.

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