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Analytical method development for determination of volatile organic compounds in calcareous desert soil

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ANALYTICAL METHOD DEVELOPMENT FOR DETERMINATION OF
VOLATILE ORGANIC COMPOUNDS IN CALCAREOUS DESERT SOIL

by

Mary F. Turner

Bachelor of Science
University of Nevada, Las Vegas
1999

A thesis submitted in partial fulfillment
of the requirements for the

Master of Science in Chemistry
Department of Chemistry
College of Science

Graduate College
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THE GRADUATE COLLEGE

We recommend that the thesis prepared under our supervision by

Mary F. Turner

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Analytical Method Development for Determination of Volatile Organic Compounds in Calcareous Desert Soil

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ABSTRACT

Analytical Method Development for Determination of Volatile Organic Compounds in Calcareous Desert Soil

by

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Soil sample preservation for volatile organic compound analysis generally requires short sample holding times or preservation of the sample's chemical constituents with sodium bisulfate (NaHSO_4). Calcareous soils cannot be preserved using NaHSO_4 because effervescence will promote the loss of analytes, and short holding times before analysis are not practical for remote sampling locations. An experimental approach was developed for determination of volatile organic compounds (VOCs) in soil that utilizes solid sorbents for sample preservation and solid-phase microextraction (SPME) sample preparation technique coupled with gas chromatography/mass spectrometry (GC/MS) for analysis. Solid sorbents are used to sequester readily extractable (vapor phase) VOCs from soil samples during sample storage. Experimental results indicate that very long sample holding times can be achieved and reasonable recoveries obtained using CarboxenTM 569 carbon molecular sieves as a soil sample preservative for carbonate soils. The method facilitates rapid sample preparation and can be easily implemented during field sampling or in the laboratory.

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CHAPTER 1

INTRODUCTION

Background

Volatile organic compounds (VOCs) are defined by the United States Environmental Protection Agency (USEPA) as a class of organic compounds such as low molecular weight aromatics, halogenated hydrocarbons, and ethers with sufficiently low boiling points to give them considerable vapor pressures at one atmosphere of pressure (USEPA Method 5035A: Closed-System Purge-and-Trap and Extraction for Volatile Organics in Soil and Waste Samples). The inherent chemical and physical properties of VOCs allow the compounds to be highly mobile and, thus, widespread in the environment (Zogorski et al., 2006). VOCs have been released into the environment from such occurrences as fuel spills, leaking underground storage tanks, and agricultural soil fumigation (Zogorski et al., 2006). Many VOCs are toxic and are suspected or known human carcinogens and hazards to aquatic organisms (Zogorski et al., 2006). Determining the concentration, as well as the distribution, of VOCs in the environment is vital to predicting their ultimate fate. As such, analysis of VOCs in soil and water remains an important activity in environmental monitoring.

The sample collection and preservation procedures in USEPA analytical methods, for VOCs in soil, have historically not been compatible with calcareous desert soil (Hewitt, 1998, Uhlerder, 2000). The acidic preservation requirements for sampling VOCs in soil, as outlined in the USEPA publication SW-846, "Test Methods for Evaluating Solid Waste, Physical/Chemical Methods", cannot be satisfied in high carbonate soil (USEPA Method 5035A). Generally, VOCs in soil and water sampled in the field are stored in

glass vials with Teflon[®]-lined silicone septa (USEPA Method 5035A). Vials containing water are completely filled to avoid the formation of a vapor bubble. With soil samples, the presence of a vapor space can usually not be avoided. In general, samples are stored cold (4 ± 2 °C) (USEPA Method 5035A) while being transported to the laboratory and analyzed within 48 hours of sample collection. Most analyses of VOCs are conducted with the federally promulgated purge-and-trap method (USEPA Method 5035A), which recommends field preservation of samples with sodium bisulfate (NaHSO₄). This reagent is added in the field, along with distilled water, to acidify the soil sample to prevent microbial degradation of VOCs. This preservation method is not practical for soils that contain carbonate minerals because resulting effervescence when the samples are acidified will cause a significant loss of analytes due to the decomposition of carbonate minerals and release of CO₂. In addition, the high buffering capacity of carbonate soils will resist acidification. The addition of water to soil will also promote the release of VOCs and thereby, exacerbate losses during storage (Minnich et al., 1996a,b). An alternative strategy of omitting preservatives and using very short holding times before analysis is not practical for remote sampling locations or for analytical labs with limited sample throughput. Therefore, alternative approaches must be explored for field preservation unless very short holding times can be tolerated or field analysis is practical.

Traditional Analytical Methods

Vapor Partitioning

Present analytical methods for VOCs in soil utilize both solvent extraction and vapor partitioning (USEPA SW-846). Static headspace and dynamic headspace (purge-and-

trap) methods, which have been adapted from water analysis, utilize the tendency of VOCs to partition into the vapor space (headspace) of a partially filled container. In static-headspace methods (USEPA Method 5021A: Volatile Organic Compounds in Various Sample Matrices using Equilibrium Headspace Analysis), VOCs are allowed to partition into the vapor phase of the container, where they can then be sampled by a gastight syringe. This method is mainly suited for the analysis of liquid or soil samples with very light molecular weight volatiles that can efficiently partition into the headspace gas volume in the sample vial (USEPA Method 5035A). Dynamic headspace analysis (USEPA Method 5035A) utilizes the sparging or purging of a soil-water suspension with an inert gas. The inert gas stream removes the VOCs from the soil matrix. The compounds are collected or trapped on a solid or polymeric sorbent and then introduced into a gas chromatograph (GC) by thermal desorption (Spraggins et al., 1981). Because the dynamic headspace method concentrates a larger fraction of the VOCs in the sample, it should be inherently more sensitive than the static method, but it is also more complicated, generally requiring several valves and a temperature programmable VOC trap; however, programming the GC to purge samples at higher temperatures allows the detection of high molecular weight compounds that aren't detectable with USEPA Method 5021A.

Solvent Extraction

An alternative to preserving soil samples by acidification (NaHSO_4) is the addition of water-soluble organic solvents such as methanol, ethanol, or acetonitrile. These solvents lower the fugacity of the VOCs and arrest microbial activity in the soil. The limitations to this approach are that the sample must be immersed in the solvent in the field and

methanol must be handled with safety precautions related to toxic, flammable liquids. An advantage of solvent extraction is the extract may be tested more than once, but the method can also increase analyte detection limits because sample dilution is required (USEPA Method 5035A). USEPA Method 5035A calls for methanol preservation in the case of high VOC concentrations (>200 ppb). This method requires extraction of VOCs from a 5-g soil sample in 10 mL of methanol. An aliquot of this extract is transferred to a vessel and diluted with 5 mL of water and then analyzed using the purge-and-trap method. Thus, solvent preservation is a practical solution if analytical instrumentation is sufficiently sensitive to compensate for sample dilution.

Alternative Preservation and Analytical Methods

Soil Desiccation

Various studies have confirmed that organic compounds can be protected from biodegradation when sorbed to soils (Bosma et al., 1997, Hatzinger and Alexander, 1995, Kelsey et al., 1997). It has been suggested that when organic compounds penetrate into soil microstructure, bacteria are sterically excluded from small pores and prevented from degrading these compounds. In many situations, the rate-determining step for biodegradation will be the diffusion of the organic compound from the soil matrix into the soil solution where microbial degradation can occur. Several studies have been conducted of vapor-soil partitioning of VOCs in calcareous soil and the role of moisture and organic carbon in vapor-soil partitioning explored (Steinberg, 1992, Steinberg and Kreamer, 1993, Steinberg et al., 1996). These investigations demonstrate that water competes with VOCs for sorption sites on soil. Thus, soil-vapor partition coefficients are

a strong function of water concentration. Previous work using both dynamic- and static-experimental methods for measuring soil-vapor partitioning of VOCs has indicated that dry Nevada Test Site (NTS) soil has a very high affinity for benzene, toluene, and other halogenated hydrocarbons. This effect has been observed by Ruiz et al., (1998) for limestone, quartz, and clay. Various other studies have confirmed the increase in VOC sorption at low soil moisture levels (Ong et al., 1992, Smith et al., 1990). Thus, under dry conditions sorption of the VOCs by soil is very high and will limit evaporative losses of VOCs from the soil matrix (Figure 1) (Steinberg, 1999). Desiccated conditions should also eliminate biological degradation of VOCs in soil samples. If water activity can be reduced in the field, VOCs would become sorbed to the soil matrix and preserved for laboratory analysis. The use of desiccants to promote soil sorption has been investigated as an alternative preservation method.

Solid Sorbent Preservation

A major loss mechanism for VOCs from soil samples is volatilization and diffusion from the sample vessel (Schumacher et al., 2000, USEPA Method 5035A). Thus, it is apparent that the distribution of VOCs in the soil, the soil-vapor, and the soil-aqueous phase is critically important. In several investigations, organic polymers have been utilized to sequester readily extractable organic compounds in soil. These polymers are of a much lower density than the soil matrix and, therefore, are easily separated from the soil by floatation. Cornelissen et al., (1997) and Chen et al., (2000) utilized Tenax™ TA beads to investigate desorption of chlorinated benzene from soil. These polymer beads were added directly to the soil and then separated after a measured contact time. The beads were subsequently extracted with hexane, and the hexane extract was analyzed for

organic target compounds. Pignatello (1990a,b) utilized Tenax™ TA for sequestering halogenated aliphatic hydrocarbons from aqueous soil suspensions. Johnson and Weber (2001) used Tenax™ to measure desorption of phenanthrene from soil. In this study, solid phases were used to sequester and preserve VOCs in the vapor phase of soil samples for environmental analysis.

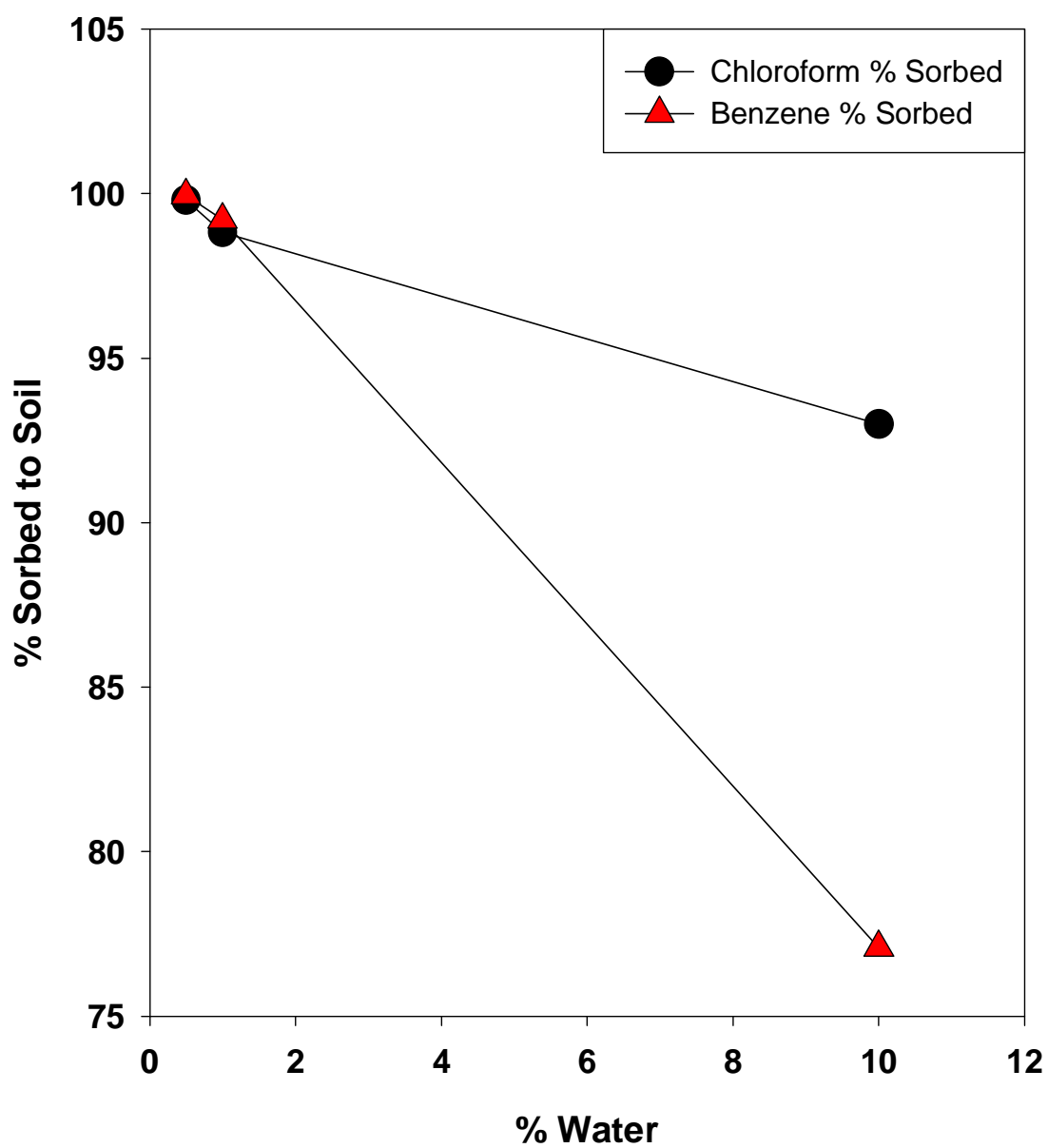


Figure 1. The effect of water on vapor-solid partitioning. Desiccation increases the partitioning of VOCs to the soil preventing evaporative loss (Steinberg, 1999).

Solid-Phase Microextraction

Solid-phase microextraction (SPME) with ion trap gas chromatography/mass spectrometry (GC/MS) for detection has been implemented as an alternative to dynamic headspace concentration to selectively extract and measure VOCs in soil (James and Stack, 1996). The method involves immersing a phase-coated fused silica fiber into the headspace of a sample container to adsorb a small fraction of the VOCs from the vapor phase. The fiber, which is mounted in a syringe needle, is subsequently transferred to the injection port of a conventional GC where the analytes are thermally desorbed onto the GC column. This method offers the advantages of reduced sample preparation time, analyte concentration, and lower detection limits. In this study, SPME-GC/MS analysis is presented as an alternative to the traditional procedures used for analysis of VOCs in soil.

Objective of Study

The objective of this study was to examine alternative sample preservation and analytical methods that would be suitable for environmental sampling of carbonate soil. Soil desiccation and sample preservation by sorption of VOCs by solid-phase adsorbents are presented as alternative methods to the traditional procedures for determining VOCs in calcareous soil. A volatile organic analysis (VOA) vial was modified to allow a solid sorbent to be held separately from the soil and to be easily removed from the sample for extraction of its volatile constituents. The SPME sample preparation technique was utilized in conjunction with GC/MS for analysis of VOCs in soil samples. A practical method was developed for implementing this technique in the field.

CHAPTER 2

EXPERIMENTAL

Solid-Phase Microextraction

The majority of the experiments were performed in 60-mL glass headspace vials (Alltech Associates) that contained either an aqueous solution or soil. For soil sorption and desiccant experiments, SPME-GC/MS analyses were performed directly on the vapor phase of the 60-mL vial. The headspace vials were crimp-sealed with aluminum caps with Teflon[®]-lined silicone septa (Alltech Associates). Silica gel was used for soil desiccation experiments. The analytes were extracted from the soil with methanol or water. Tenax[™], activated charcoal, graphitized carbon, and carbon molecular sieves were used for solid-sorbent preservation experiments. The analytes were desorbed from the solid phases with either 1.0 mL of pyridine or 1.0 mL of methanol. Better results were obtained using pyridine for extractions from the carbon molecular sieves but the reason is not understood. Initially, the pyridine signal in the GC was very large and interfered with the analysis. Acidification of the solution with H₂SO₄ protonated the pyridine and suppressed its concentration in the vapor phase. For all the experiments, sufficient headspace (15 to 50 mL) was available above the samples for vapor-phase equilibration.

SPME sampling was performed after adjusting the sample temperature to 25 °C. Temperature control was achieved by placing the 60-mL headspace vial into a water-jacketed beaker that was connected to a circulating temperature bath (Cole-Parmer Model 1268-02). The internal diameter of this beaker matched the external diameter of the 60-mL vial so that good thermal contact was achieved. Water samples contained a Teflon[®]-

coated magnetic stir-bar. The samples were all stirred at 300 rpm using a magnetic stir motor equipped with a digital tachometer (VWR model 400S). Sample agitation enhances analyte extraction and reduces extraction time by increasing mass transfer rates and promoting equilibration with the vapor phase. A 100- μm (film thickness) polydimethylsiloxane (PDMS) fiber (Supelco) was selected for routine VOC analysis. A 75- μm CarboxenTM/PDMS fiber (Supelco) was tested that had greater sensitivity for VOC sorption than the 100- μm PDMS fiber, but this fiber was more fragile and had persistent analyte carryover problems. Most of the experimental work was done with the 100- μm PDMS fiber because it was relatively rugged, had little analyte carryover, and had sufficient sensitivity and analyte selectivity. The fibers were conditioned before use by heating them in the injection port of the GC at 250 °C for 1 hour. The conditioning of the fiber is to release any monomers in the glue that is used to attach the fiber to the syringe needle. Some initial extraneous peaks from the glue may be observed during the preliminary blank analysis of the syringe fiber. Sample temperature was monitored with a digital thermometer. When the sample reached temperature equilibrium, the SPME syringe needle was inserted through the septum of the sample vial. The fiber was exposed to the headspace above the sample and allowed to equilibrate for 10.0 minutes. The equilibration time was determined by performing a series of experiments varying the fiber equilibration time until the analyte recovery plateaus. After the analyte adsorbed to the fiber, the fiber was retracted into the needle. The needle was withdrawn from the sample vial and immediately transferred to the GC injection port for the analyte desorption process (Figure 2).

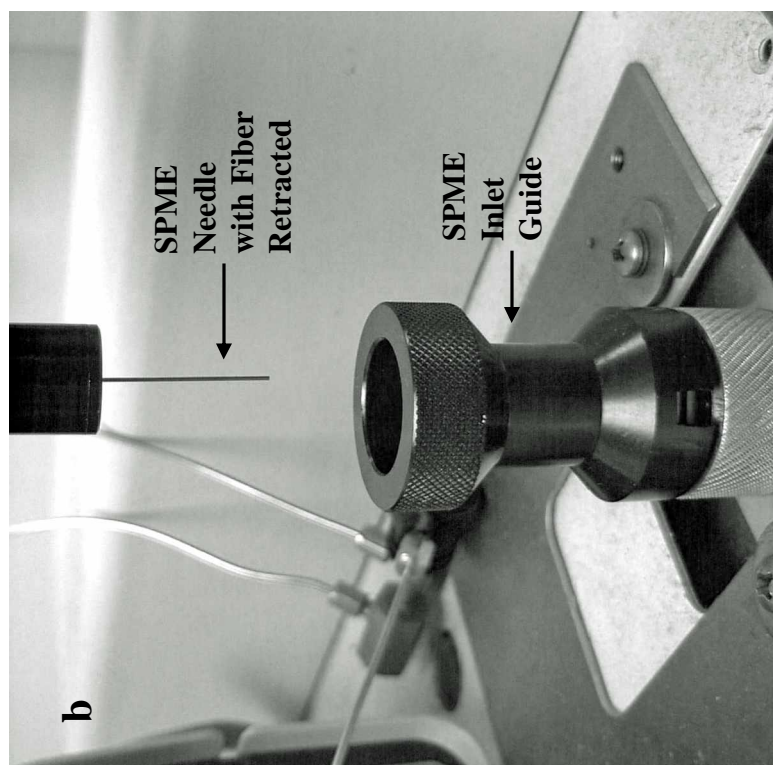
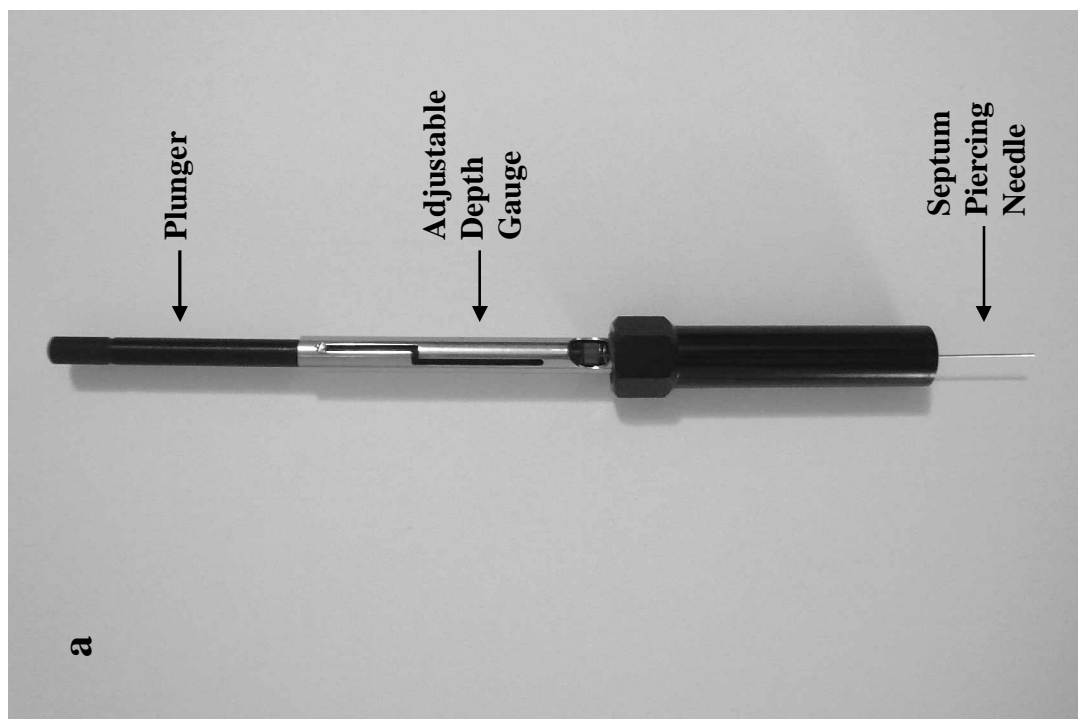


Figure 2. (a) SPME fiber holder (b) SPME sample introduction to GC injection port

GC Conditions and Analysis

Chromatographic analysis was performed using a Varian Star 3400 Gas Chromatograph interfaced with a Varian Saturn III ion trap mass spectrometer. The GC was equipped with a JADE™ valve (Alltech Associates) on the injector. The JADE™ valve uses a magnetic check valve to seal the GC injector instead of the conventional silicone septum. With the JADE™ valve system, a magnetic ball that normally prevents the loss of carrier gas is pushed from the injector port by the syringe needle used for injection. When the needle is removed, the magnetic seal is pulled back into place resealing the injector. The transfer line and injector temperatures were held at 280 °C and 270 °C, respectively. The ion trap temperature was adjusted to 170 °C. The mass spectrometer was tuned and mass calibrated with FC-43 using the automated methods designed by the manufacturer. The mass scan range was 50 to 450 at 0.5 s/scan. Separations were performed on a Supelco EC-1 (30 m x 0.25 mm i.d., film thickness 0.25 µm) capillary column. Column head pressure was 10 psi.

Response factors for various VOCs were determined with an external standard added to a 60-mL headspace vial containing 25 mL of 3 M NaCl. The NaCl increases the ionic strength of the solution and in turn reduces the solubility of the analytes, enhancing their extraction in the headspace (Schwarzenbach et al, 1993). The concentration of NaCl used in the experiments was determined by adding a known concentration of VOC standard solution to 25-mL NaCl solutions of increasing ionic strength and measuring the analytes in the vapor phase by SPME-GC/MC analysis (Figure 3). The standard solution was prepared by adding 10-µL volumes of each target analyte to 10 mL of methanol in a screw-cap flask. The analytes were then quantified using single ion chromatograms

corresponding to the parent ion of the mass spectrum (Figures 4-8). The vapor phase of the septum-sealed vial was sampled using the SPME fiber (10.0 min at 25 °C), and the fiber was thermally desorbed in the GC injector.

The GC conditions were as follows (Table 1). The initial column temperature was 40 °C. The door of the oven was opened during the injection procedure and the air-circulating fan was turned off. Cryo-focussing of the VOC analytes was accomplished by immersing an approximately 10-cm loop of the capillary column in a small (6 oz) Styrofoam[®] cup filled with liquid nitrogen. All injections were made in the splitless mode. The SPME fiber was inserted into the GC injector and the column program was started with the oven door open and the liquid nitrogen in place. During the first 5 minutes of the analysis, the oven door remained open, and the liquid nitrogen remained in place to concentrate the VOCs released from the fiber in the cooled loop of the column. After 5 minutes, the cup was quickly removed, the oven door immediately closed, and the oven fan reactivated. The oven was held at 40 °C for an additional 7 minutes and then ramped at a rate of 15 °C/min to a final temperature of 250 °C. This injection technique was simple to implement and highly reproducible. Chromatographic retention times were observed to vary by less than 0.1% using this injection approach. The analytes used in this study were chloroform, benzene, trichloroethylene (TCE), and toluene. Their detection limits are reported in Table 2. Detection limits were a function of the background concentrations of the volatile compounds, the instrument sensitivity, and the fiber sampling conditions. SPME efficiency for headspace sampling is highly dependent on temperature conditions. Optimization of these conditions is discussed below.

Table 1. Summary of GC/MS operating conditions

Parameter	Conditions
Mass Range	50 to 450 m/z
Scan time (1 μ Scans)	0.500 seconds
Initial column temperature	40 °C
Initial hold time	7.0 min
Column ramp rate	15 °C/min
Final column temperature	250 °C
Final hold time	2.0 min

Table 2. Detection limits of target analytes

Compound	Detection Limits (μg/L)
Chloroform	0.0033
Benzene	0.010
Trichloroethylene	0.0018
Toluene	0.0002

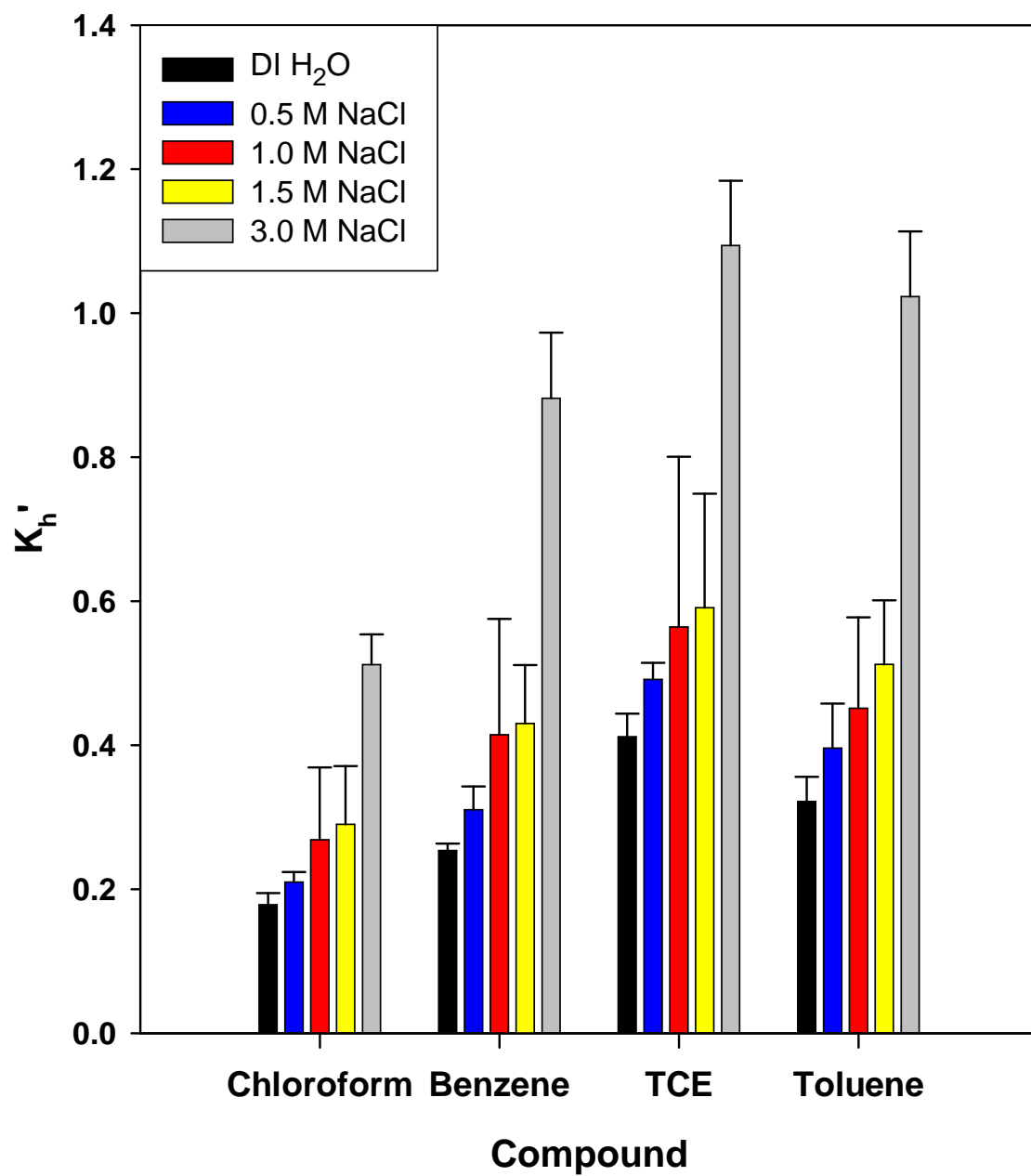


Figure 3. Dimensionless Henry's Law as a function of ionic strength.

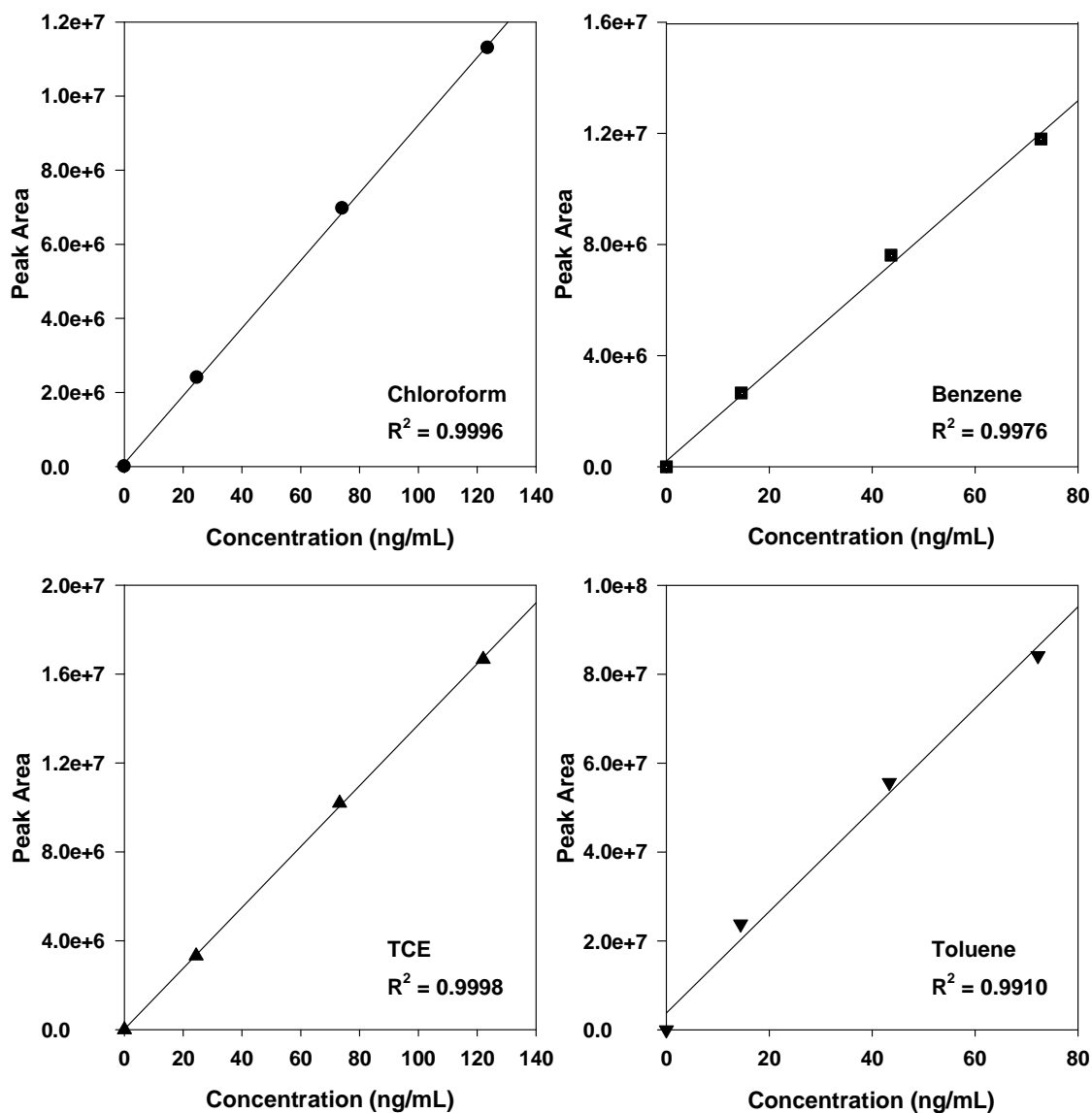


Figure 4. Example of SPME fiber calibration using a standard solution prepared with chloroform, benzene, TCE, and toluene. The analytes were quantified using single ion chromatograms corresponding to the parent ion of the mass spectrum.

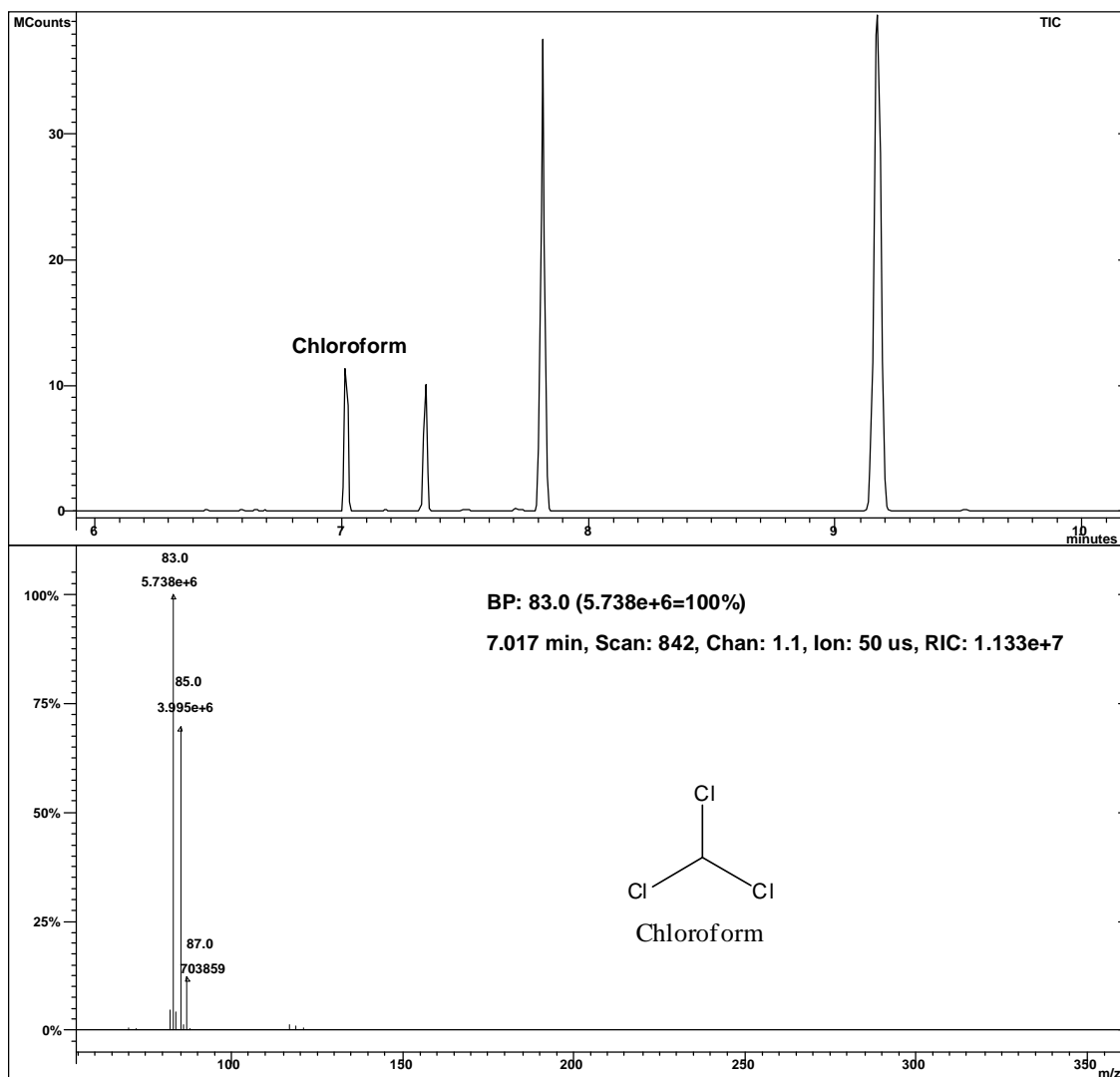


Figure 5. GC/MS chromatogram of chloroform (4.45 μg) (m/z 83) calibration standard analyzed with a 100- μm polydimethylsiloxane SPME fiber.

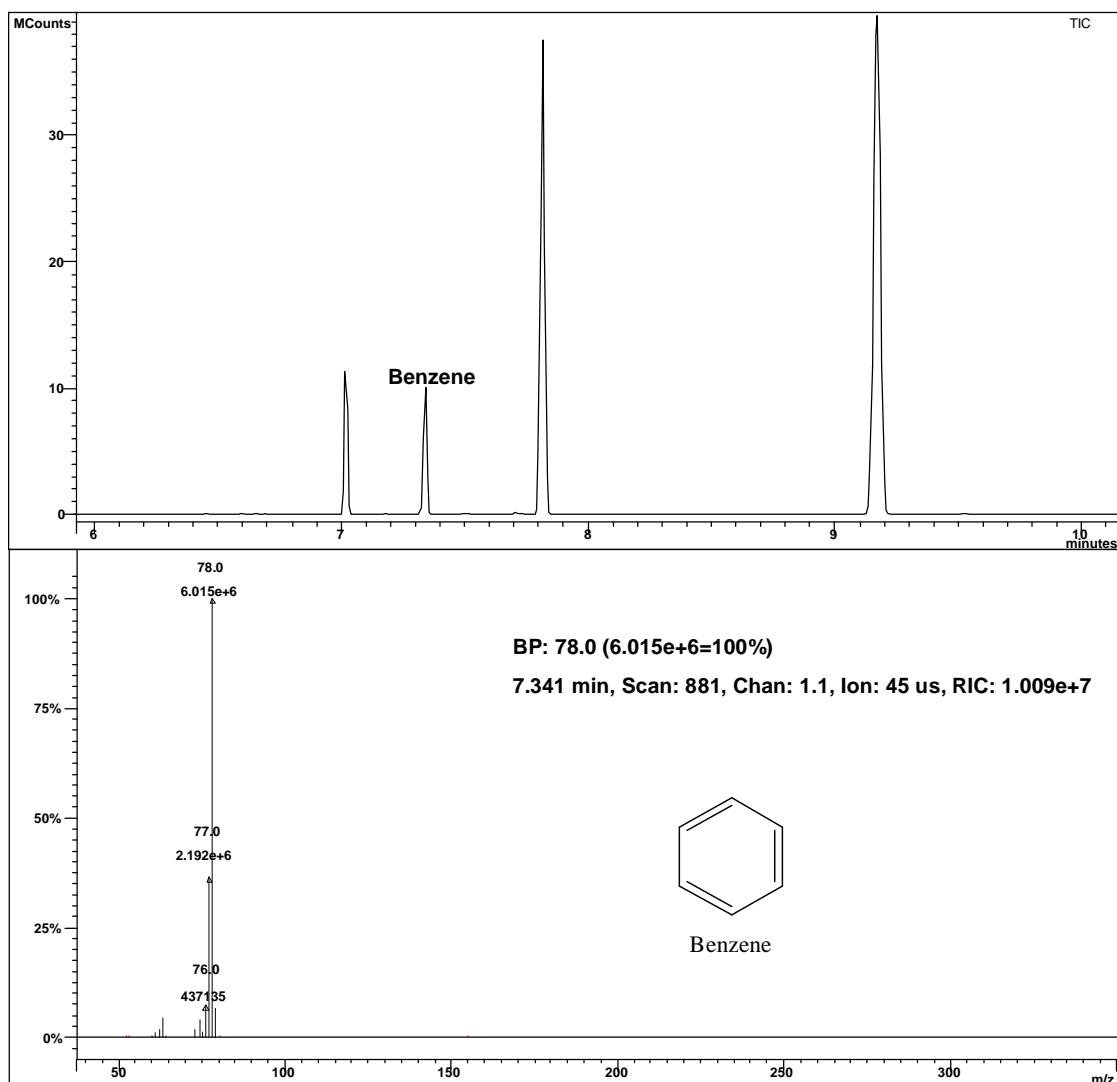


Figure 6. GC/MS chromatogram of benzene (2.62 μg) (m/z 78) calibration standard analyzed with a 100- μm polydimethylsiloxane SPME fiber.

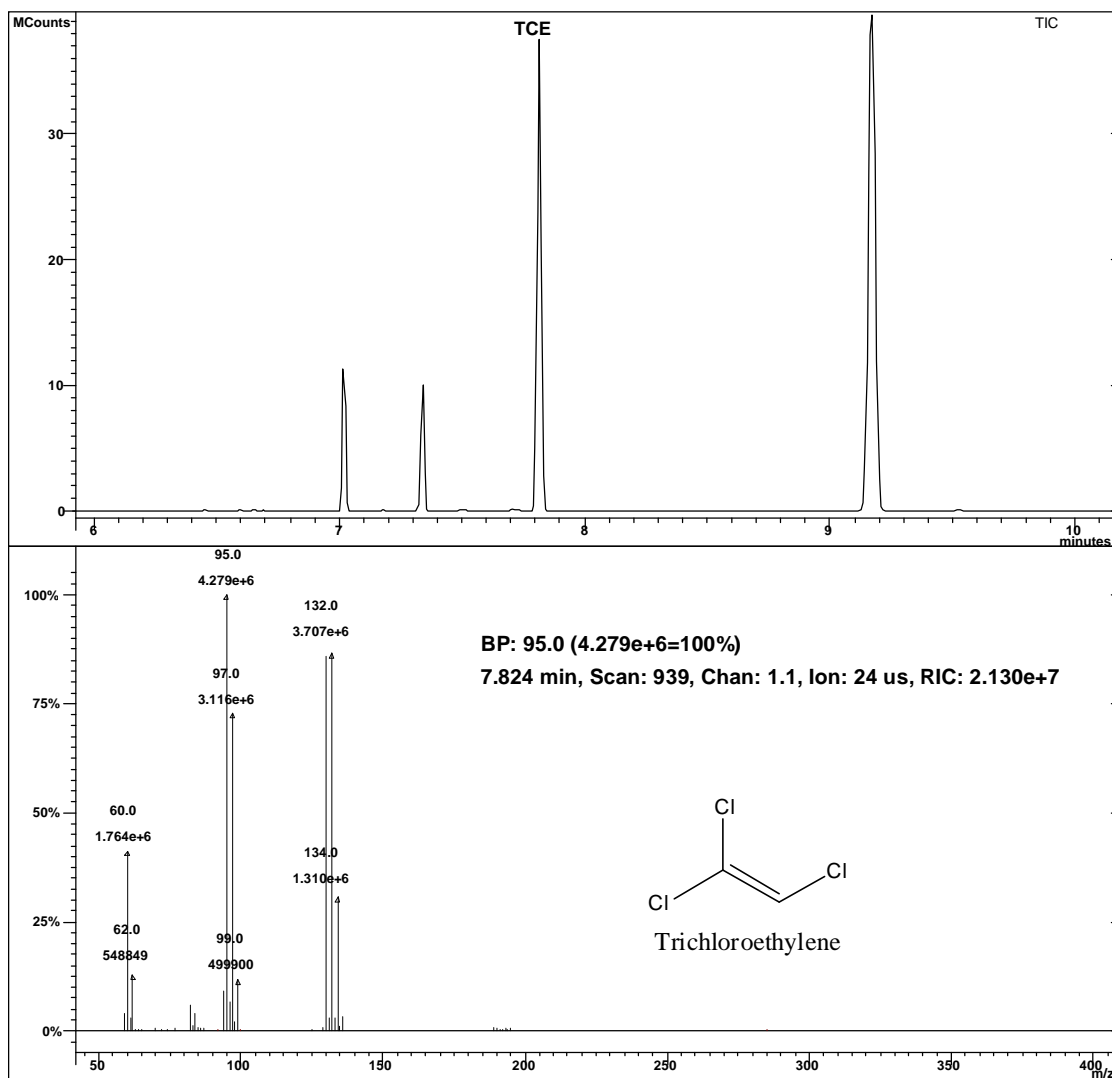


Figure 7. GC/MS chromatogram of TCE (4.39 μg) (m/z 132) calibration standard analyzed with a 100- μm polydimethylsiloxane SPME fiber.

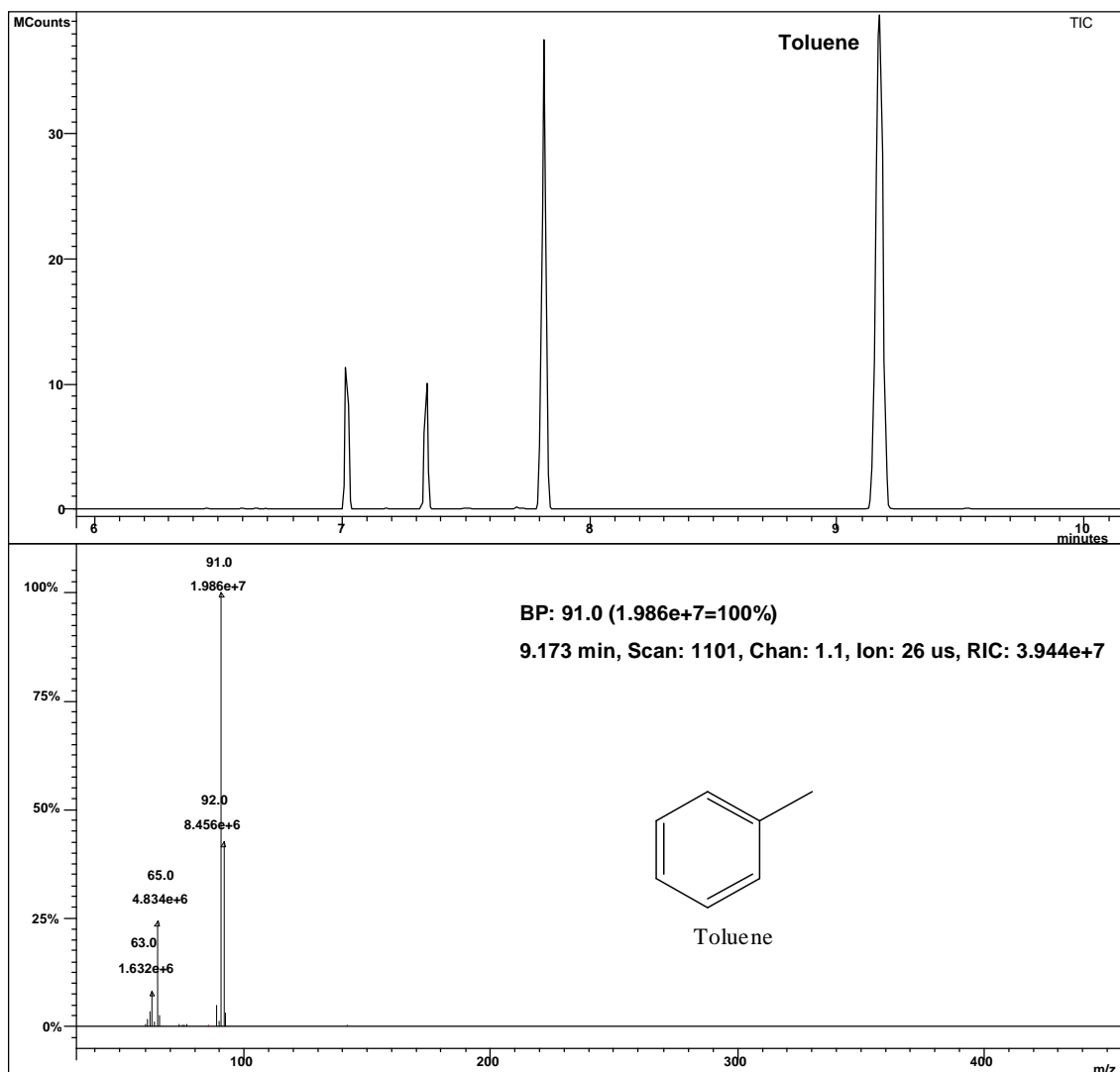


Figure 8. GC/MS chromatogram of toluene (2.60 μg) (m/z 91) calibration standard analyzed with a 100- μm polydimethylsiloxane SPME fiber.

Optimization of SPME Conditions

The extraction efficiency is determined by the partitioning of the analyte between the water and the vapor and the vapor and the fiber (K_f). Because the volume (V_f) of the fiber is small, the amount of analyte the fiber coating adsorbs and introduces into the GC is directly proportional to the concentration in the vapor phase (C_v). The amount of analyte removed by the fiber does not significantly reduce the total concentration of analyte in the sample or disturb other equilibria such as vapor-liquid or vapor-solid.

In general, the amount of analyte injected (n_{inj}) is given by (Potter and Pawliszyn, 1992):

$$n_{inj} = K_f * V_f * C_v \quad (1)$$

where, K_f (dimensionless) is the fiber/vapor partition coefficient.

Experiments at various temperatures indicate the n_{inj} increases as the equilibration temperature decreases (the enthalpy of adsorption onto the fiber is negative). On the other hand, the concentration of an analyte in the presence of an aqueous phase (C_{aq}) is a function of the Henry's law constant (K_h) for the analyte. The dimensionless Henry's law is given by:

$$K_h' = \frac{C_v}{C_{aq}} \quad (2)$$

The equilibrium constant K_h generally increases (for volatile organic compounds) with temperature, resulting in an increased concentration of analyte in the vapor phase (Schwarzenbach et al, 1993). Combining these two relationships for a sample containing a known amount of analyte (n_t), a known volume of aqueous phase (V_w), and a known volume of vapor (V_g) results in:

$$n_{inj} = \frac{K_f * V_f}{1 + \frac{V_w}{V_g} * \frac{1}{K_h}} * \frac{n_t}{V_g} \quad (3)$$

This equation shows the influence of the fiber-vapor partition coefficient and the Henry's law constant on the amount of analyte injected. An increase in temperature affects the two partition coefficients in opposite ways. For volatile aromatic and halogenated hydrocarbons, the detection limits were observed to be more sensitive to the value of K_f than the Henry's law coefficient and sensitivity increased with a decrease in temperature (Table 3) (Figures 9 and 10).

For most of this study, SPME sample equilibration was performed at 25 °C. This temperature was selected because it was close to laboratory temperature and shortened equilibration times. Sensitivity at this temperature, although not at a maximum, was adequate for this study. Lower temperatures could be used to achieve lower detection limits for samples with very low VOC concentrations.

Table 3. Analyte peak area as a function of temperature (chloroform 4.45 µg, benzene 2.62 µg, TCE 4.39 µg, and toluene 2.60 µg).

Temp (°C)	Chloroform (peak area)	Benzene (peak area)	TCE (peak area)	Toluene (peak area)
10	4334695	1784107	5475852	53256682
15	3759649	1659372	5417449	47200208
20	2475208	1142484	3375201	36348164
24	2509558	1012233	3117032	32912504
30	1853532	655546	2195385	22847289

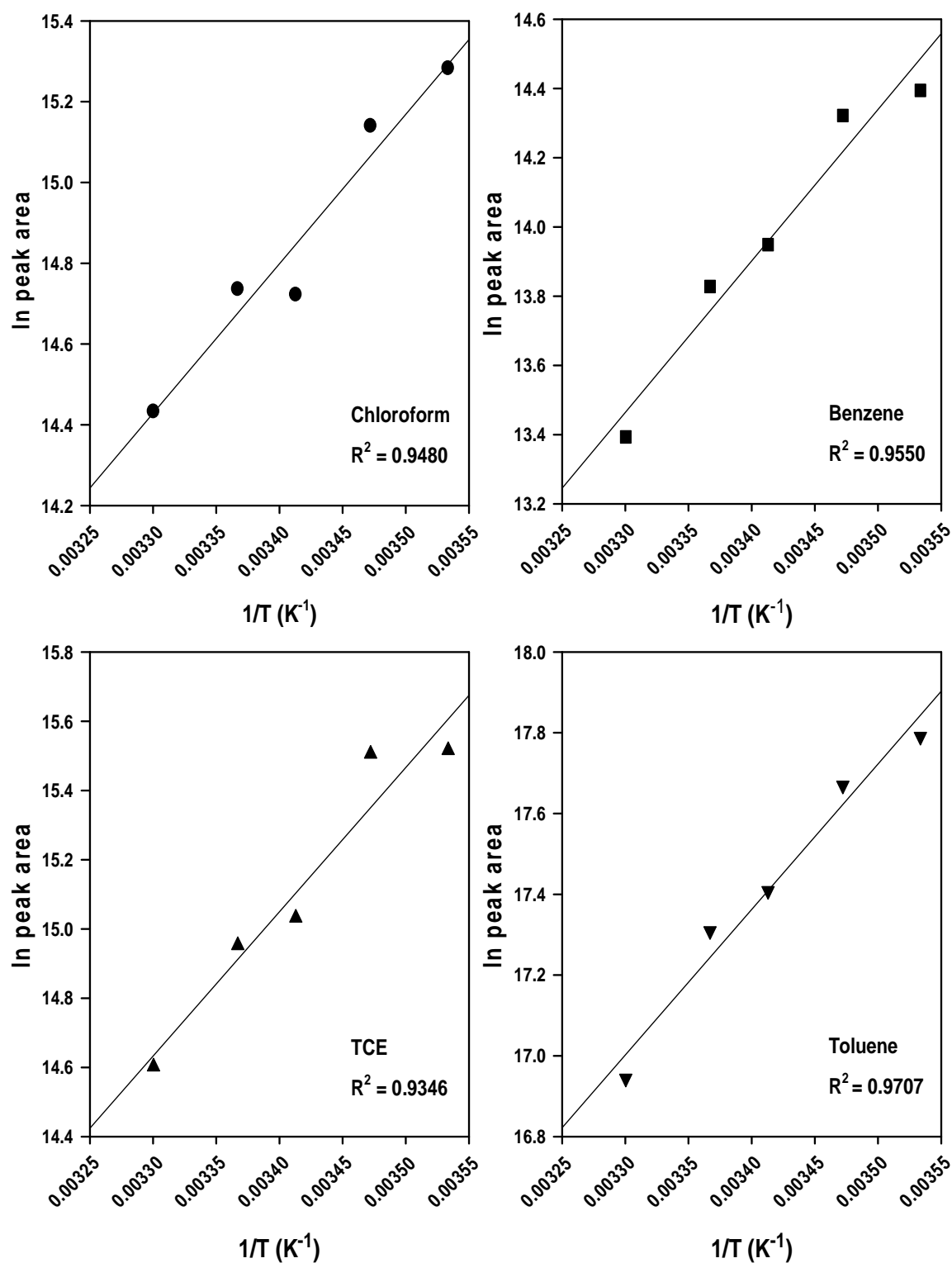


Figure 9. Effect of temperature on SPME vapor-fiber partitioning.

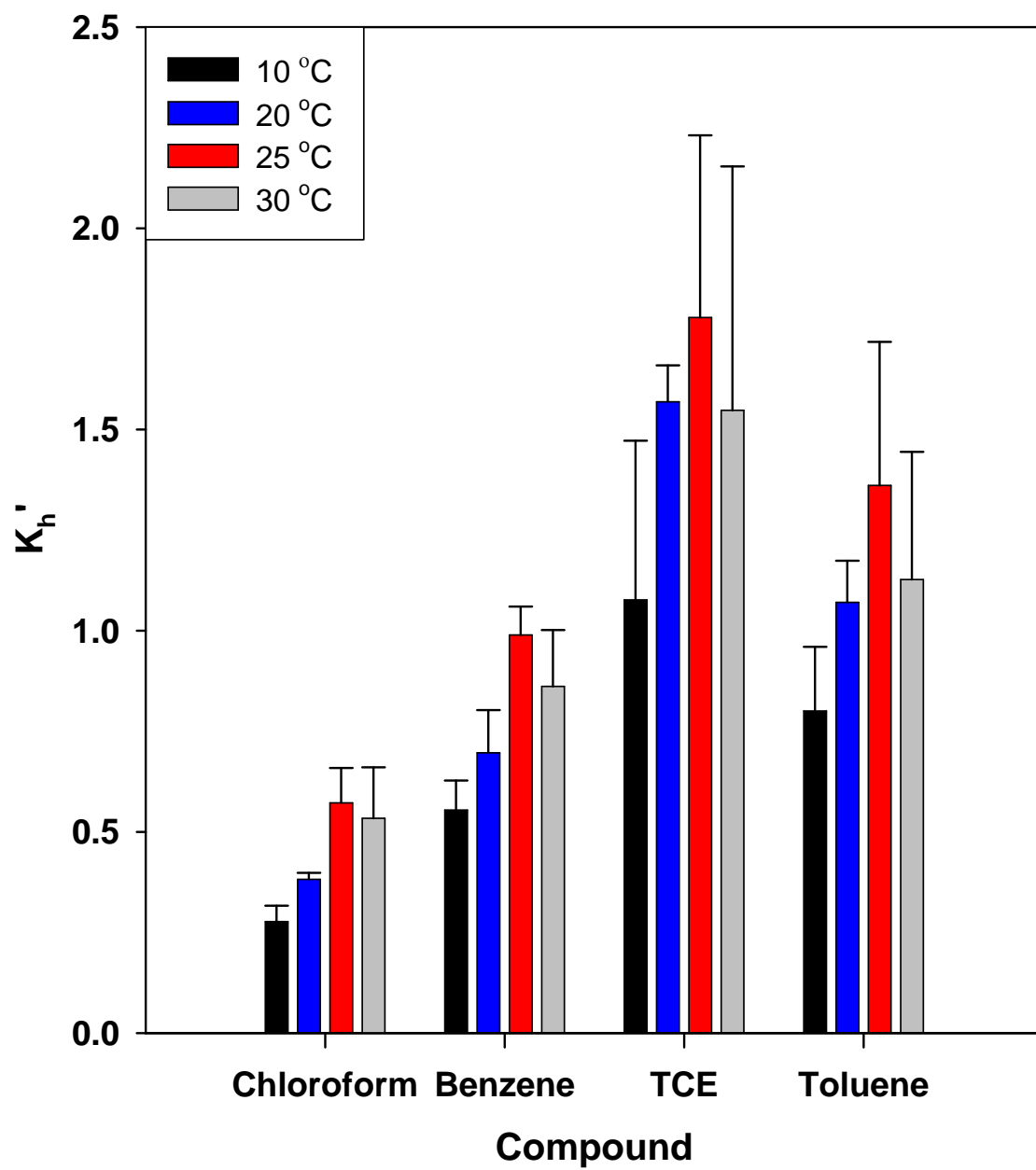


Figure 10. Dimensionless Henry's Law as a function of temperature.

Materials

Silica Gel was purchased from J.T. Baker (100/200 mesh). Tenax™ TA (60/80 mesh) and activated charcoal (SK-4, type C, 80/100 mesh) were purchased from Alltech Associates. Carboxen™ 569 (20/45) and Carbotrap™ (20/40) were obtained from Supelco. Before use, the desiccant and sorbents were heated at 200 °C for 24 hours under a stream of nitrogen gas.

Methanol was distilled-in-glass grade and obtained from Burdick and Jackson. Pyridine (Gold Label) was obtained from Sigma-Aldrich and distilled before use. The VOCs (Table 4) were purchased from Sigma-Aldrich and Burdick and Jackson.

Table 4. Properties of compounds used in sorption experiments (CRC, 1994)

Compound	Formula	Formula Weight (g/mol)	Density, 25 °C, (g/mL)	Boiling Point °C	Vapor Pressure, 25 °C, Torr
Chloroform	CHCl ₃	119.38	1.4800	61	195
Benzene	C ₆ H ₆	78.11	0.8729	80	95.3
TCE	CHCl=CCl ₂	131.39	1.4578	87	74
Toluene	C ₆ H ₅ CH ₃	92.14	0.8647	111	29
Methanol	CH ₄ O	32.04	0.7872	65	127.5
Pyridine	C ₅ H ₅ N	79.10	0.9786	115	32.3

The primary objective of this study was to optimize a sampling and analytical method for calcareous desert soils. Two soils of this type were obtained. The first soil, called

Las Vegas surface soil, was obtained from a Nevada Department of Transportation construction site located at the intersection of North Las Vegas Boulevard and East Lake Mead Boulevard, Las Vegas, Nevada. The second soil was collected from Area 26 of the Nevada Test Site (NTS). The mineralogy and texture of these soils are similar to soil previously characterized from Area 5 of the NTS (Tan, 2002) (Table 5). As a contrast, VOC recoveries from the calcareous desert soils were compared to recoveries from a highly organic soil (Pahokee peat) obtained from the International Humic Substances Society (IHSS) (St. Paul, Minnesota) and a commercial volatile organic analyte (VOA) contaminated soil standard from Resource Technology Corporation (RTC) (Laramie, Wyoming). Soil surface areas were measured (after drying at 200 °C) by N₂ adsorption using a Micromeritics Gemini Model 2350. Organic carbon was measured by high temperature combustion in oxygen under static conditions using an Exeter model CE-440 elemental analyzer. Carbonate content was determined by selective dissolution analysis. This method is based on the reaction of hydrochloric acid (HCl) with soil carbonates and the observance and measurement of the loss of CO₂ from the sample (United States Salinity Laboratory Staff, 1954). Soil samples were prepared in triplicate for analysis. Oven-dried (110 °C) soil was transferred to centrifuge tubes and weighed (~10 g each). Twenty-five mL of 0.1 N HCl was added to each tube. When the effervescence subsided (~20 min.), the samples were centrifuged for 10 minutes at 2000 rpm and rinsed 3 times with distilled H₂O. After each addition of H₂O, the centrifuge tube was swirled, and the soil was allowed to settle for 10 minutes. The samples were put in an oven to dry at 110 °C for 24 hours. The samples were removed from the oven, cooled, and the weight of CO₂ lost by the soil was recorded. The carbonate detection limit was determined by the

precision of sample weights with an estimated error of $\pm 0.1\%$. Soil surface area, organic carbon content, and carbonate content are reported in Table 5.

Table 5. Summary characteristics of soil

Soil Type	Surface Area (m ² /g)	Organic Carbon (%)	Carbonate (%)
NTS Area 5	19.6	0.04 \pm 0.01	1.58 \pm 0.08
Las Vegas	6.74	2.44 \pm 0.20	1.45 \pm 0.30
NTS Area 26	14.2	0.05 \pm 0.01	0.843 \pm 0.126
Pahokee peat	0.866	45.70 ¹	ND ²
RTC VOA	9.62	0.53 \pm 0.12	1.42 \pm 0.01

¹IHSS

²not detectable

Soil Sample Preservation Methods

Soil Desiccation

Silica gel was evaluated as a soil sample desiccant. Silica gel, a synthetic amorphous form of silicon dioxide (mesh size 100/200), is a highly porous inert material with a large surface area (800 m²/g) and high adsorption efficiency for water vapor (J. T. Baker). The soil sample can be stored in the field with silica gel to lower the soil moisture and increase VOC partitioning into the solid phase (soil). Soils used for these studies were air-dried, sieved to pass 0.85 mm mesh, and then oven dried for 24 hours at 110 °C. Samples were prepared by adding 5 g of soil to 60-mL headspace vials. A known volume of distilled water was added to the soil with a 1-mL glass syringe to give a

moisture content of 5% to 15% by weight. Each vial was sealed with a rubber plug and then shaken by hand until the water was uniformly distributed in the soil. The soil samples were allowed to equilibrate with the water for two hours after which silica gel desiccant (5 g) was added directly to the soil surface in the sample vials. The samples were spiked with a known concentration of VOC standard solution (0.9 to 1.5 $\mu\text{g/g}$ of soil), and the vials were quickly crimp-sealed with an aluminum cap with a Teflon[®]-lined silicone septum. After 24 hours, the vials were opened and the VOCs extracted from the soil by adding 10 mL of water directly to the 60-mL headspace vial. The vials were resealed and the samples analyzed by SPME-GC/MS as described above.

Solid Sorbent VOC Sequestration

Tenax[™] TA, activated charcoal, Carbotrap[™], and Carboxen[™] 569 (Table 6) were investigated as VOC sequestering agents for soil samples. Solid sorbents introduced into a soil sample will absorb VOCs from the gas phase. During sample storage, VOCs in the soil sample ideally should be transferred to the sorbent thus preventing evaporative losses. Many solid sorbents have pore structures that are considerably smaller (5-20 Å) than most soil microbes (0.2-2.0 μm), thus, sorption should prevent microbial decomposition as well. For example, the pore diameters for Carboxen[™] 569 are 5-8 Å; therefore, most of the surface area of the Carboxen[™] 569 (485 m^2/g) is internal (Supelco Product Information) and inaccessible to soil microbes. In this study, the solid sorbent was separated from the soil in either a glass vial or a porous stainless-steel tube. This approach allowed the sorbent, with the adsorbed VOCs, to be easily separated from the soil sample and the VOC content to be extracted or desorbed and measured by SPME-GC/MS.

Table 6. Summary characteristics of sorbents (Supelco and Alltech Associates)

Sorbent	Description	Mesh Size	Density (g/mL)	Pore Diameter (Å)	Surface Area (m ² /g)
Tenax™ TA	Porous polymer based on 2,6-diphenylene oxide	60/80	0.25	2000	35
Activated Charcoal Type C	Coconut shell based	80/100	~0.45	0-20	~1100
Carbotrap™	Graphitized carbon black	20/40	0.37	Non-porous	100
Carboxen™ 569	Carbon molecular sieve	20/45	0.58	5-8	485

Experiments were conducted with the solid sorbents in 2-mL glass screw-cap vials. The vials were inserted into 60-mL headspace vials that contained soil samples. The soils used in these experiments were air-dried, sieved (0.85-mm mesh), and oven-dried at 110 °C for 24 hours. In general, 5-g soil samples were weighed into the 60-mL headspace vials and a known volume of distilled water was added to each sample with a 1-mL glass syringe to give a moisture content of 5% to 15% by weight. The vials were sealed with a rubber plug, and the soils were shaken by hand until the water was homogeneously distributed. The hydrated samples were then allowed to equilibrate for 2 hours. Solid sorbent (100-400 mg) was weighed into a small 2-mL screw-cap vial. The small vial was sealed with a holed cap that contained a stainless-steel mesh septum. The 2-mL vial was then inserted “upright” into the 60-mL vial and the soil was spiked with a VOC standard in methanol. The VOC spiking levels were generally in the range of 0.9 to 1.5 µg/g of soil. Each 60-mL vial was then crimp-sealed with an aluminum cap with a

Teflon[®]-lined silicone septum and remained sealed for 24 hours. At the completion of the experiments, the inner vial was retrieved by an attached copper wire, and the VOCs were extracted from the solid sorbent with 1 mL of an organic solvent (methanol or pyridine). A small amount of solvent (50 to 100 μ L) was removed from the sample vial with a syringe and then injected into 25 mL of 3M NaCl in a 60-mL headspace vial that contained a Teflon[®]-coated magnetic stir-bar. The vial was crimp-sealed with a Teflon[®]-lined silicone septum and the sample analyzed by the SPME-GC/MS procedure described above (Schematic 1) (Figure 11).

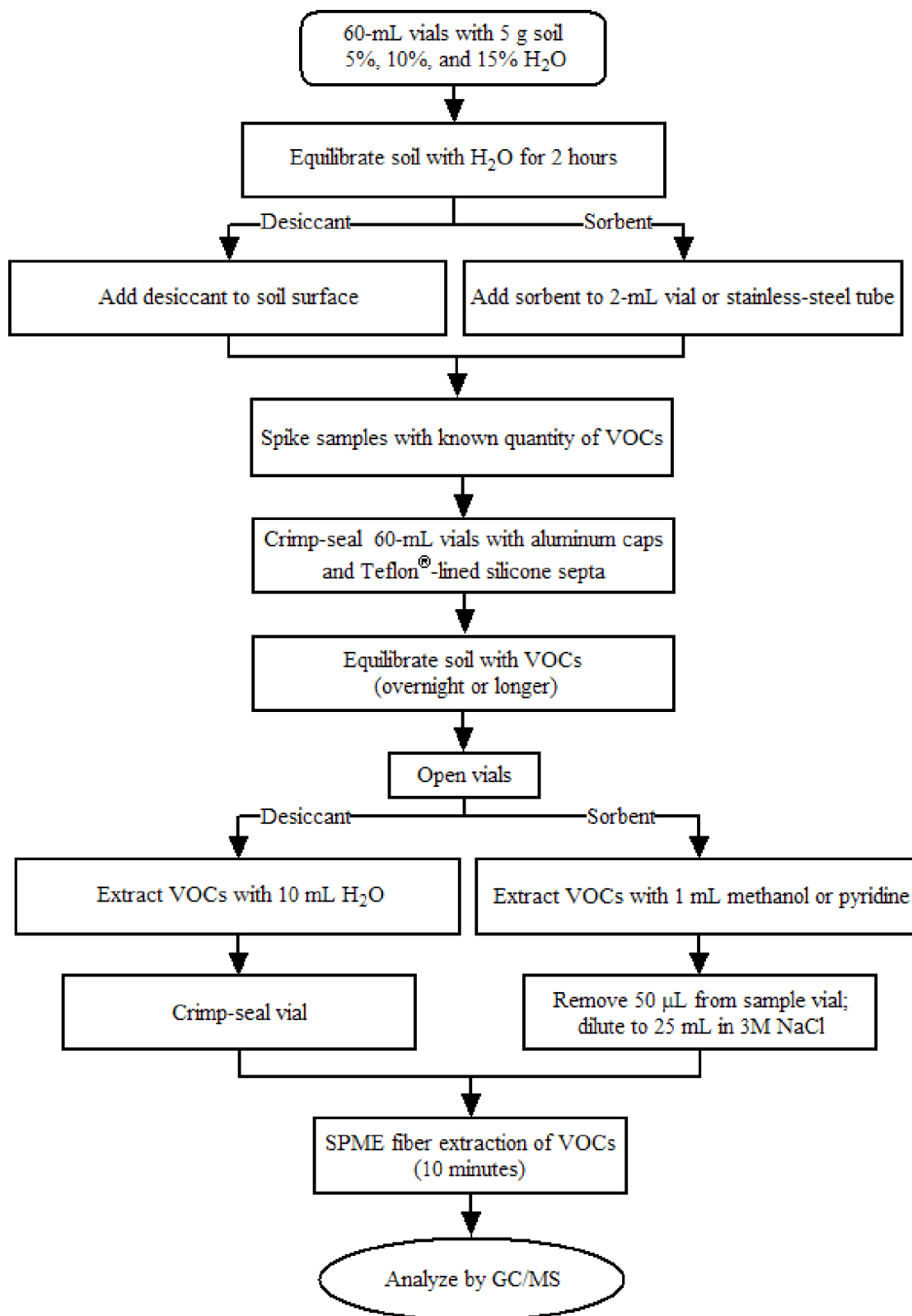
Modified VOA Vial

Because the preliminary approach would be difficult to implement during field sampling, a modified 40-mL VOA vial was designed for use with the solid-sorbent preservation method. This vial incorporates a machined Teflon[®] plug to replace the usual silicone septum. This plug was held in place using a holed VOA vial cap. A good seal was assured by incorporating a Teflon[®]-coated silicone o-ring between the glass vial and the Teflon[®] plug. A hole was drilled in the Teflon[®] plug and a hollow porous stainless-steel tube was inserted into the plug. The solid sorbent was placed into the porous tube and held in place with a piece of silanized glass wool.

The Teflon[®] plug was machined from Teflon[®] stock (2.54 cm d.) that was purchased from McMaster-Carr. The Teflon[®]-coated silicone o-rings (17.5 mm i.d., 2.38 mm width) were purchased from McMaster-Carr as well. The 40-mL VOA vials and holed caps were obtained from Alltech Associates. Porous stainless-steel tubing was purchased from Mott Corporation and cut into 3.81-cm lengths. Porous stainless-steel tubing with

20- and 40- μ m nominal pore diameters was tested; no influence on trapping efficiency was observed.

The soils used in these experiments were air-dried, sieved (0.85-mm mesh), and oven-dried at 110 °C for 24 hours. In general, 5-g soil samples were weighed into the 40-mL VOA vials and a known volume of distilled water was added to each sample with a 1-mL glass syringe to give a moisture content of 5% to 15% by weight. The vials were sealed with a screw cap and the soils were shaken by hand until the water was homogeneously distributed. The hydrated samples were then allowed to equilibrate for 2 hours. Solid sorbent (100-400 mg) was weighed and placed into the stainless-steel tube. The soil was spiked with a VOC standard in methanol. The cap with the Teflon[®] plug with the stainless-steel tube and sorbent were put into place on the vial, and the vial was sealed for 24 hours. The samples were analyzed by the SPME-GC/MS procedure described above. A picture of the modified VOA vial is shown in Figure 12.



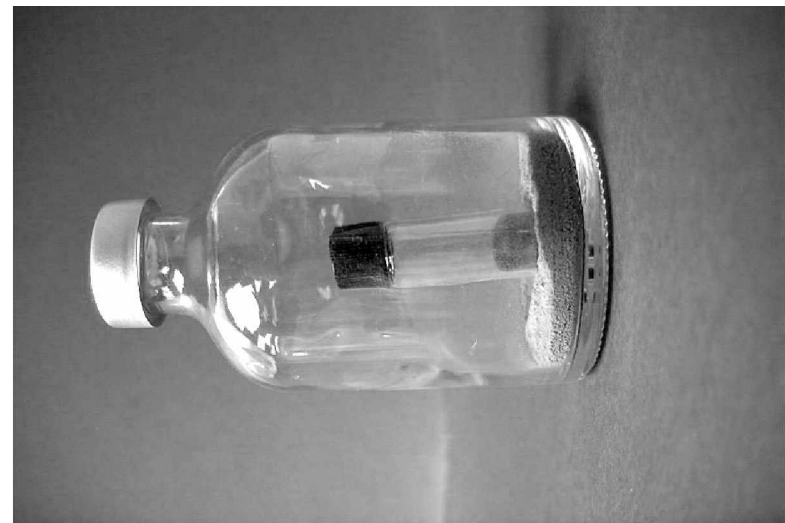
Schematic 1. Procedure for sample preparation, VOC extraction, and SPME-GC/MS analysis.



Silica Gel Desiccant



Tenax™ TA



Carbon Molecular Sieves

Figure 11. Representative sample vials used in method development.

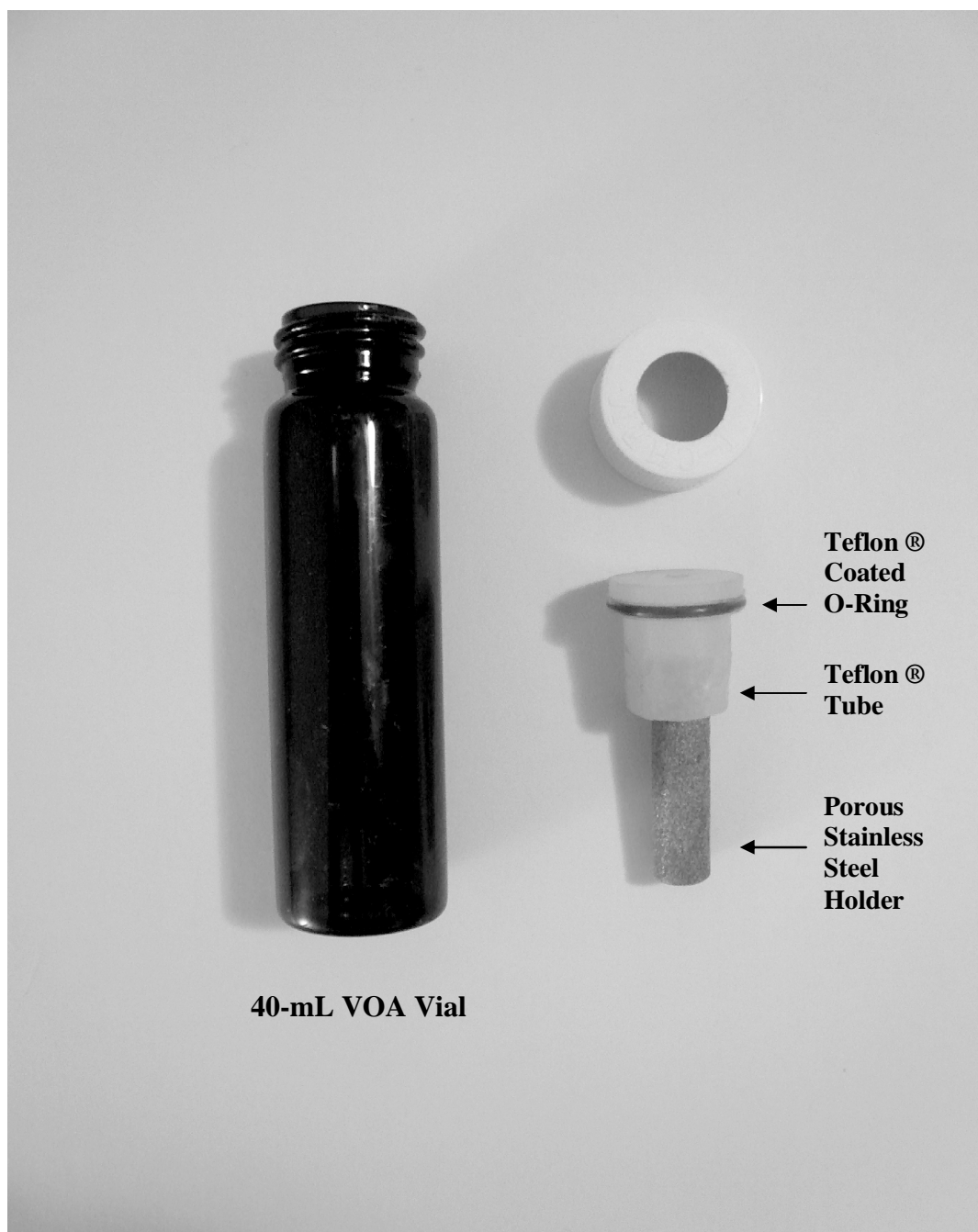


Figure 12. Modified VOA Vial for solid-sorbent preservation. Vial cap contains a porous stainless-steel tube to hold 100 to 300 mg of solid sorbent. Soil sampled in the field is placed in the vial and the solid sorbents absorb VOCs from the gas phase during sample storage.

CHAPTER 3

RESULTS AND DISCUSSION

The objective of this study was to examine alternative sample preservation and analysis methods for VOCs in high carbonate soil samples. Silica gel, a commonly used desiccant, and activated charcoal, Tenax™ TA, Carbotrap™, and Carboxen™ 569, commercially available solid-phase sorbents, were investigated as VOC sequestering agents.

Soil Desiccation

Silica Gel

Table 7 and Figure 13 show the average VOC recoveries for Silica Gel desiccant in Las Vegas soil samples with moisture levels of 5%, 10%, and 15% by weight. Silica gel desiccant was added to the soil surface (5 g Silica gel/5 g soil) in the 60-mL headspace vials, and the samples were spiked with 7.42, 4.37, 7.32, and 4.33 µg of chloroform, benzene, TCE, and toluene, respectively. The vials were sealed and the samples stored for 24 hours at room temperature. The VOCs were extracted from the soil by adding 10 mL of water directly to the vial and measured by the SPME-GC/MS procedure described above. No significant trend in VOC recoveries with water content was observed.

Table 7. Average VOC recoveries for soil preserved with Silica Gel desiccant.

Soil % Moisture	Chloroform % Recovery	Benzene % Recovery	TCE % Recovery	Toluene % Recovery
5	59.2 ± 1.03	75.5 ± 2.26	77.1 ± 8.42	62.4 ± 5.74
10	57.2 ± 6.79	68.9 ± 7.70	86.2 ± 12.0	53.1 ± 6.10
15	59.2 ± 0.21	66.8 ± 1.06	74.4 ± 10.6	57.4 ± 1.20

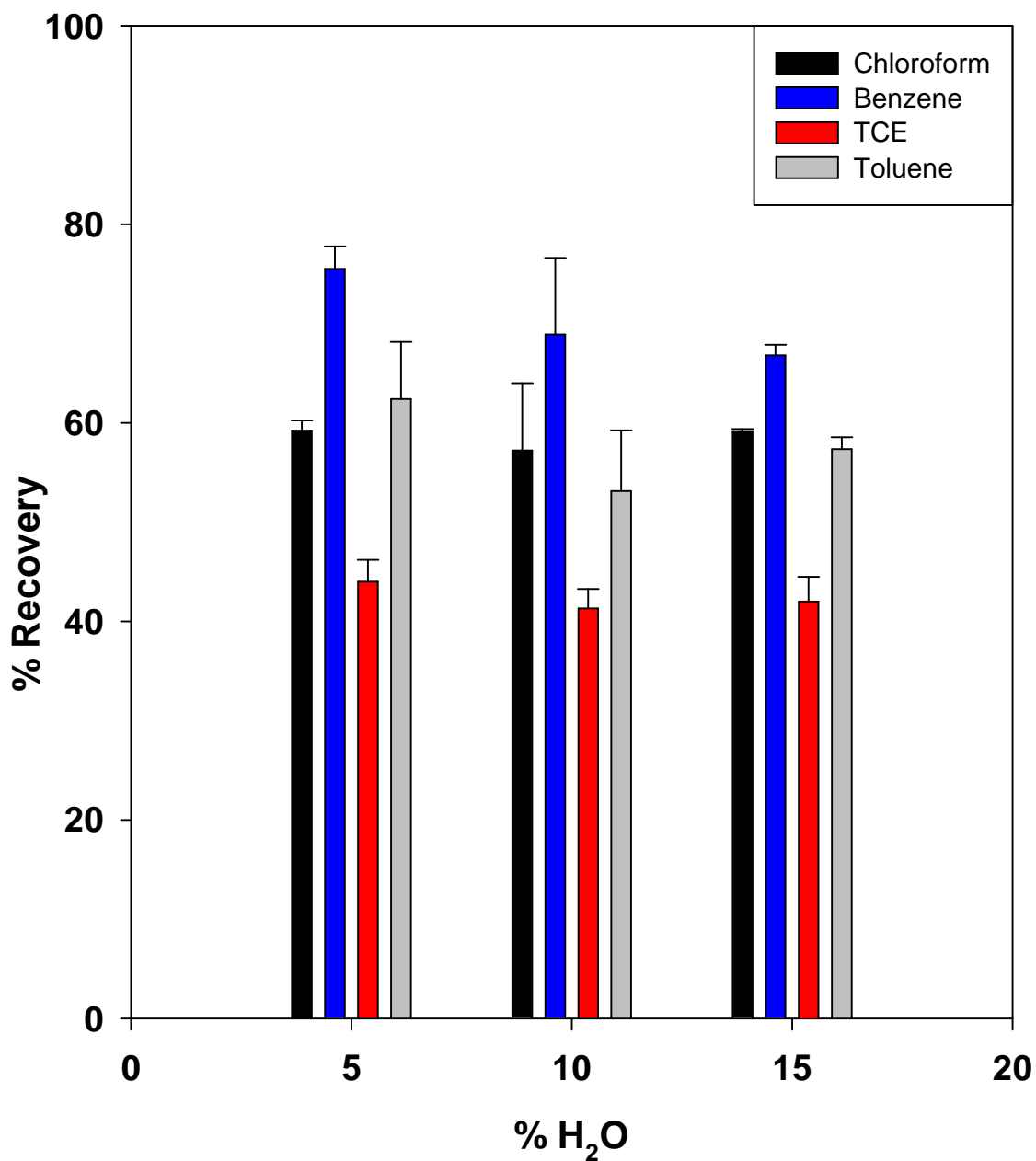


Figure 13. Summary of average VOC recoveries for Silica Gel desiccant in Las Vegas soil samples (5 g/5 g soil) with 5%, 10%, and 15% water content. VOC recoveries were by addition of 10 mL of water directly to the desiccant/soil mix in the headspace vial.

Solid Sorbent VOC Sequestration

Tenax™ TA

Tenax™ TA is a porous polymer resin that has been specifically designed for the trapping of volatile and semi-volatile compounds from air or that have been purged from liquid or solid sample matrices (Scientific Instrument Services, SKC Gulf Coast, Inc., Alltech Associates, Inc.). Las Vegas soil samples (5 g) with soil moisture levels of 5%, 10%, and 15% by weight were prepared. Tenax™ TA (200 mg) was added to an open 2-mL glass vial sealed with a holed cap containing a stainless-steel mesh septum and the vial was inserted upright onto the soil surface inside the 60-mL headspace vial. The soil samples were spiked with 7.42, 4.37, 7.32, and 4.33 µg of chloroform, benzene, TCE, and toluene, respectively. The vials were sealed and samples stored for 24 hours at room temperature. The VOCs adsorbed to the Tenax™ TA resin were desorbed in 1 mL of methanol and the methanol extract analyzed by the SPME-GC/MS method outlined above. VOC recoveries for all three moisture levels were similar. The results for the three moisture levels were combined and the average VOC recoveries for Tenax™ TA are shown Table 8 and Figure 14. The recoveries for all analytes were consistent and reproducible but low (37% to 58%).

Table 8. Average VOC recoveries for soil preserved with Tenax™ TA.

Analyte	Analyte Added (µg)	% Recovery
Chloroform	7.42	45.8 ± 3.16
Benzene	4.37	41.5 ± 4.62
TCE	7.32	37.2 ± 3.78
Toluene	4.33	57.5 ± 4.40

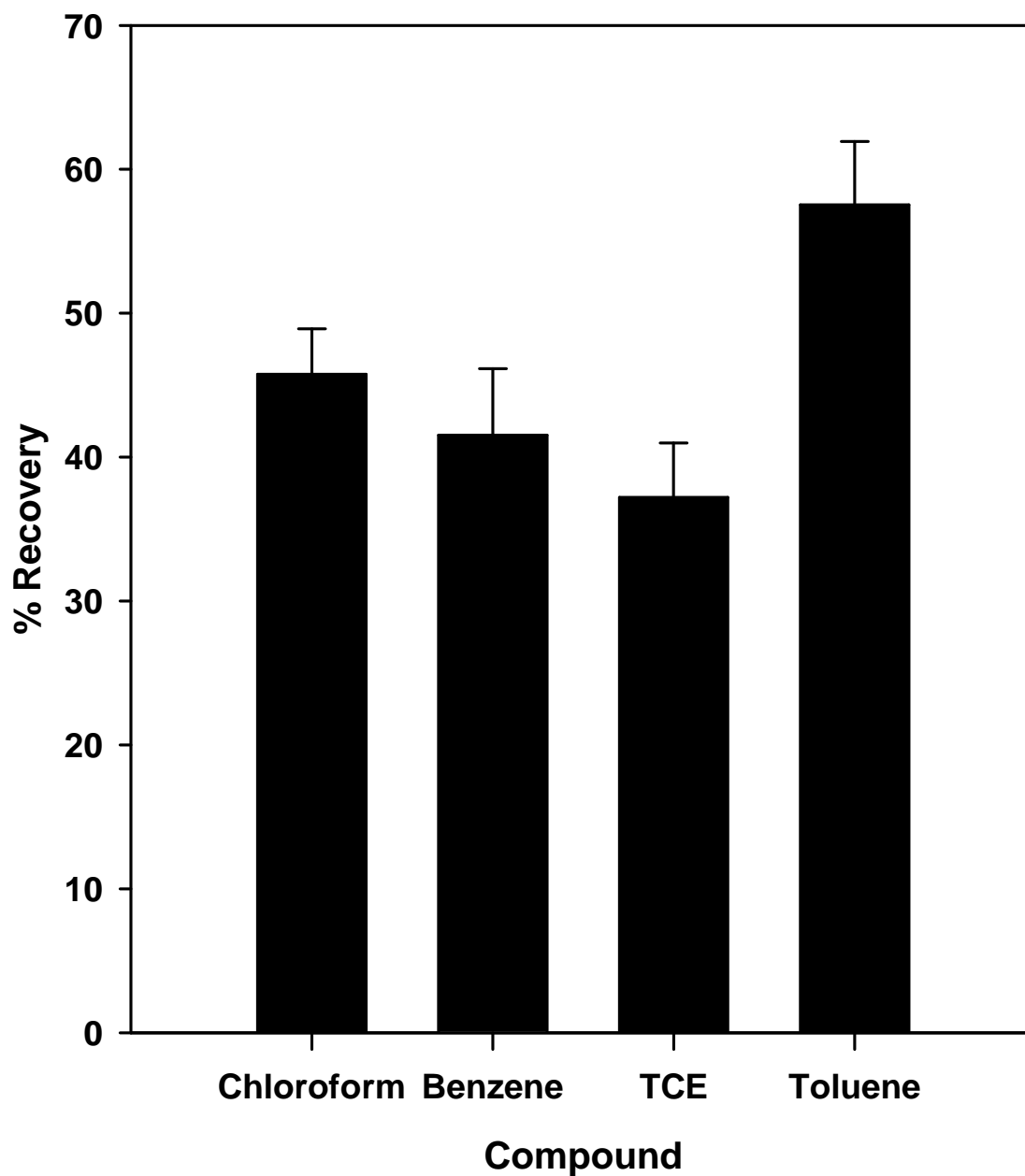


Figure 14. Summary of average VOC recoveries from Tenax™ TA (200 mg) for sorbent experiments using Las Vegas soil samples (5 g) with 5%, 10%, and 15% water content. The VOC recoveries for all moisture levels were similar and the combined results are shown. VOC recoveries were in methanol.

Activated Charcoal

Because activated charcoal is frequently used to adsorb VOCs from ambient air, a type C charcoal obtained from Alltech Associates (SK-4) was tested for use in this method (SKC Gulf Coast Inc.). Las Vegas soil samples (5 g) with soil moisture levels of 5%, 10%, and 15% by weight were prepared. Activated charcoal (10 mg) was added to an open 2-mL glass vial sealed with a holed cap containing a stainless-steel mesh septum and the vial was inserted upright onto the soil sample surface inside the 60-mL headspace vial. The soil samples were spiked with 7.42, 4.37, 7.32, and 4.33 μg of chloroform, benzene, TCE, and toluene, respectively. The vials were sealed and samples stored for 24 hours at room temperature. The analytes were extracted from the charcoal with 1 mL of methanol and analyzed by the SPME-GC/MS method previously described. VOC recoveries for all three moisture levels were similar and the results were combined for the average VOC recoveries shown in Table 9 and Figure 15. The recoveries for benzene (22.2%) and toluene (7.63%) were significantly low with this material and likely reflect poor extractability from charcoal using methanol.

Table 9. Average VOC recoveries for soil preserved with charcoal.

Analyte	Analyte Added (μg)	% Recovery
Chloroform	7.42	64.5 ± 8.89
Benzene	4.37	22.2 ± 3.32
TCE	7.32	43.3 ± 6.88
Toluene	4.33	7.63 ± 2.22

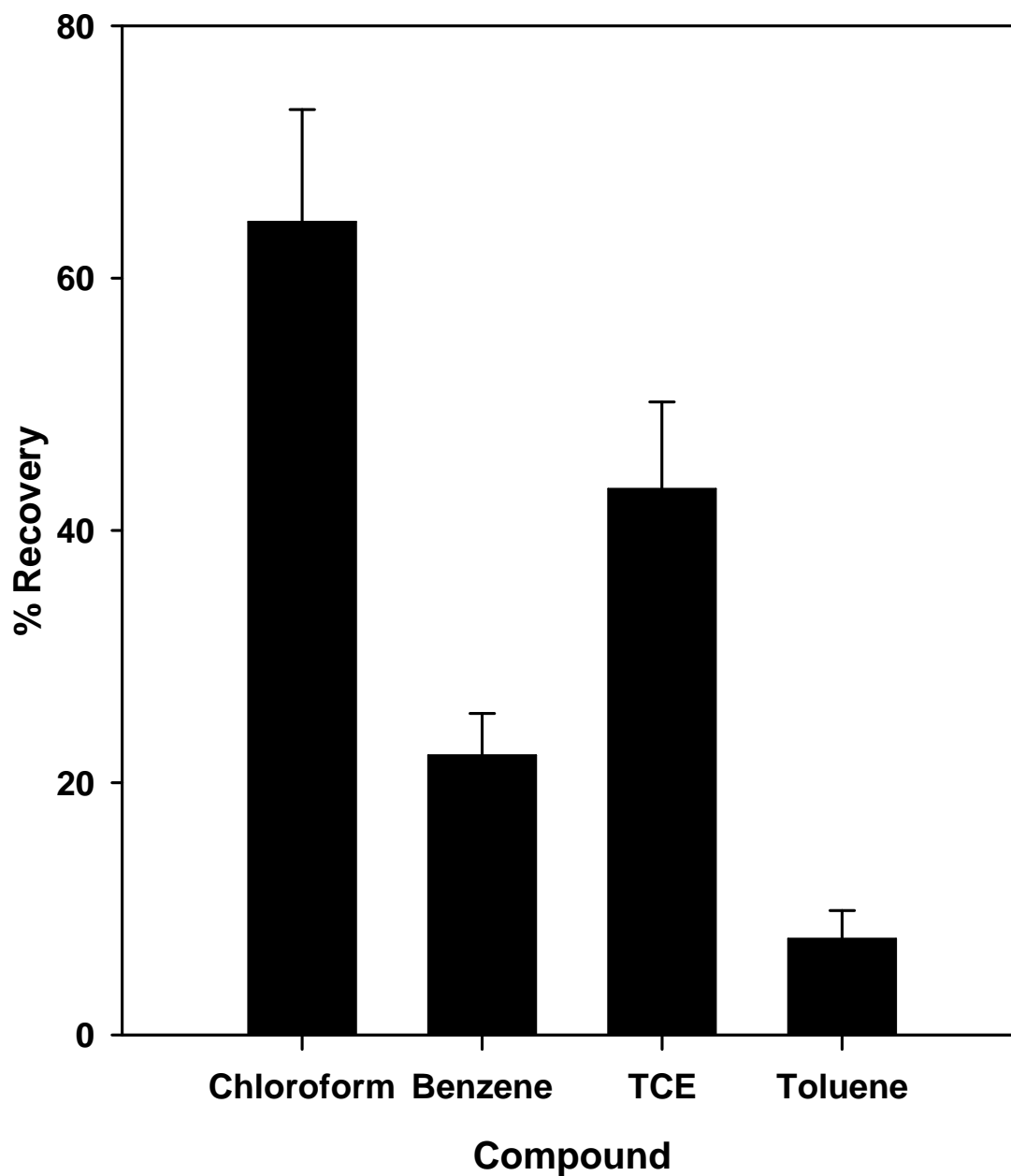


Figure 15. Summary of average VOC recoveries from charcoal (10 mg) for sorbent experiments using Las Vegas soil samples (5 g) with 5%, 10%, and 15% water content. The recoveries for all moisture levels were similar and the combined results are shown. VOC recoveries were in methanol.

Carbotrap™

Carbotrap™ is graphitized carbon black that is frequently used for trapping VOCs from ambient air (Supelco). Carbotrap™ adsorbent has no surface ions or active functional groups. It is unaffected by humidity and not susceptible to solvent degradation (Supelco). The average results for Carbotrap™ tests are summarized in Table 10 and Figure 16. In these experiments, Las Vegas soil samples (5 g) with soil moisture levels of 5%, 10%, and 15% by weight were prepared. Carbotrap™ (250 mg) was added to an open 2-mL glass vial sealed with a holed cap containing a stainless-steel mesh septum and the vial was inserted upright onto the soil surface inside the 60-mL soil sample vial. The soil samples were spiked with 7.42, 4.37, 7.32, and 4.33 µg of chloroform, benzene, TCE, and toluene, respectively. The vials were sealed and samples stored for 24 hours at room temperature. The analytes were extracted with pyridine solvent (1 mL) and analyzed by the SPME-GC/MS method. The VOC recoveries for all three moisture levels were similar and the results were combined. This phase was not utilized on a routine basis because recoveries exceeding 100% (116% to 135%) could not be explained by fiber blanks or contamination of extraction solvent.

Table 10. Average VOC recoveries for soil preserved with Carbotrap™

Analyte	Analyte Added (µg)	% Recovery
Chloroform	7.42	115.7 ± 5.750
Benzene	4.37	134.6 ± 6.136
TCE	7.32	125.4 ± 7.018
Toluene	4.33	127.1 ± 13.43

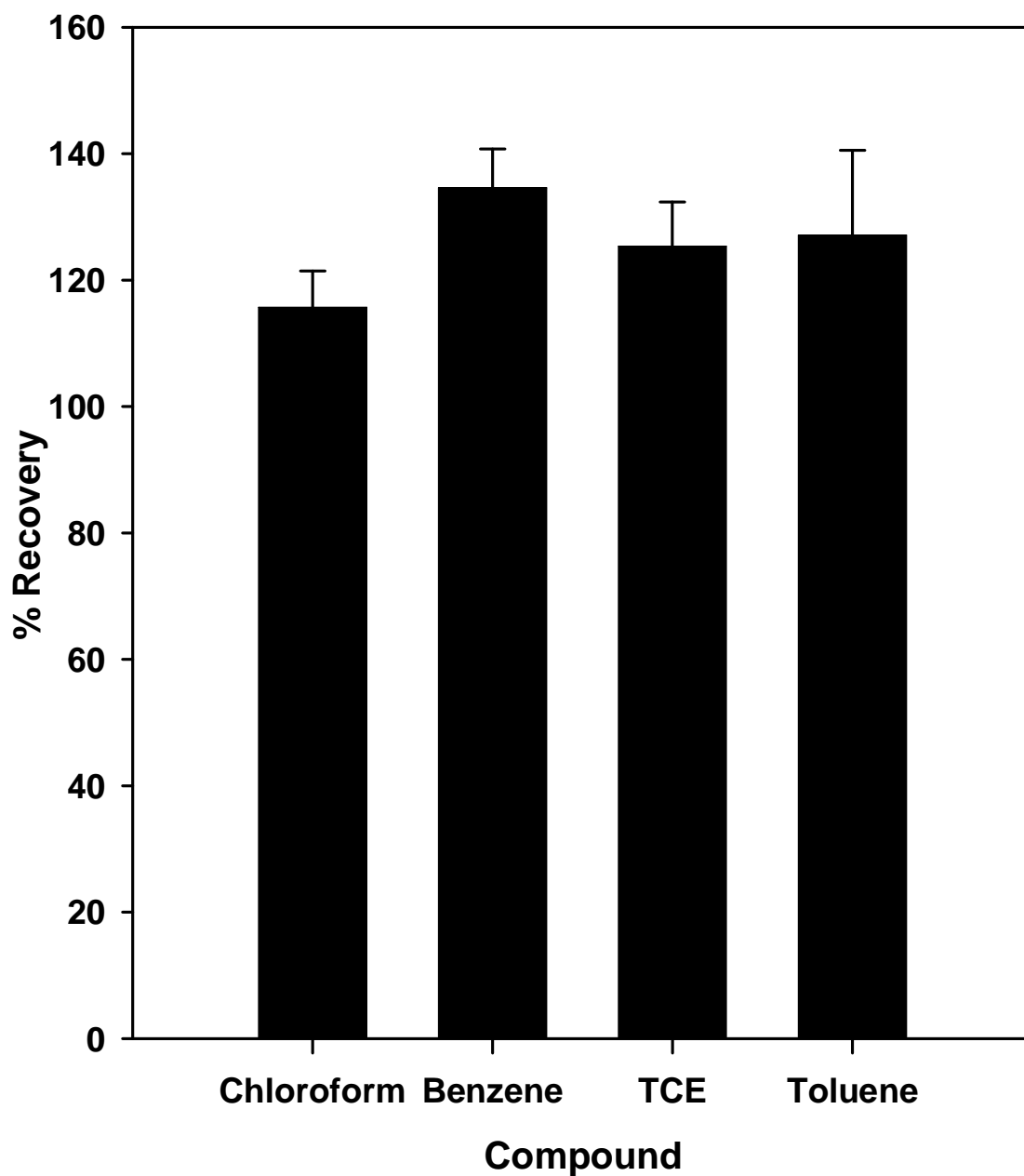


Figure 16. Summary of average VOC recoveries from Carbotrap™ (200 mg) for sorbent experiments using Las Vegas soil samples (5 g) with 5%, 10%, and 15% water content. The recoveries for all moisture levels were similar and the combined results are shown. VOC recoveries were in pyridine.

Carboxen™ 569

The majority of the experimental work was performed with Carboxen™ 569 carbon molecular sieve adsorbent resin. This resin has a large mesh size (20/45) and high surface area (485m²/g) as well as a low affinity for water (Supelco). The large mesh size of the material favors interparticle diffusion within the trap, while the large surface area with small pore diameters (5 to 8 Å) enhances adsorption of compounds of small molecular size (Supelco). The average results for Carboxen™ 569 experiments are summarized in Table 11 and Figure 17. NTS Area 26 soil samples (5 g) with soil moisture levels of 5%, 10%, and 15% by weight were prepared. Carboxen™ 569 (200 mg) was added to an open 2-mL glass vial sealed with a holed cap containing a stainless-steel mesh septum and the vial was inserted onto the soil surface inside the 60-mL headspace vial. The soil samples were spiked with 7.42, 4.37, 7.32, and 4.33 µg of chloroform, benzene, TCE, and toluene, respectively. The vials were sealed and samples stored for 24 hours at room temperature. The VOCs were extracted from the Carboxen™ 569 with 1 mL of pyridine and analyzed by the SPME-GC/MS procedure described above. No significant trend in VOC recoveries with water content was observed and the results for the three moisture levels were combined. VOC recoveries for all analytes were consistent and reproducible. Carboxen™ 569 was selected for further experiments.

Table 11. Average VOC recoveries for soil preserved with Carboxen™ 569.

Analyte	Analyte Added (µg)	% Recovery
Chloroform	7.42	69.0 ± 4.96
Benzene	4.37	59.4 ± 2.01
TCE	7.32	48.9 ± 3.47
Toluene	4.33	55.5 ± 2.85

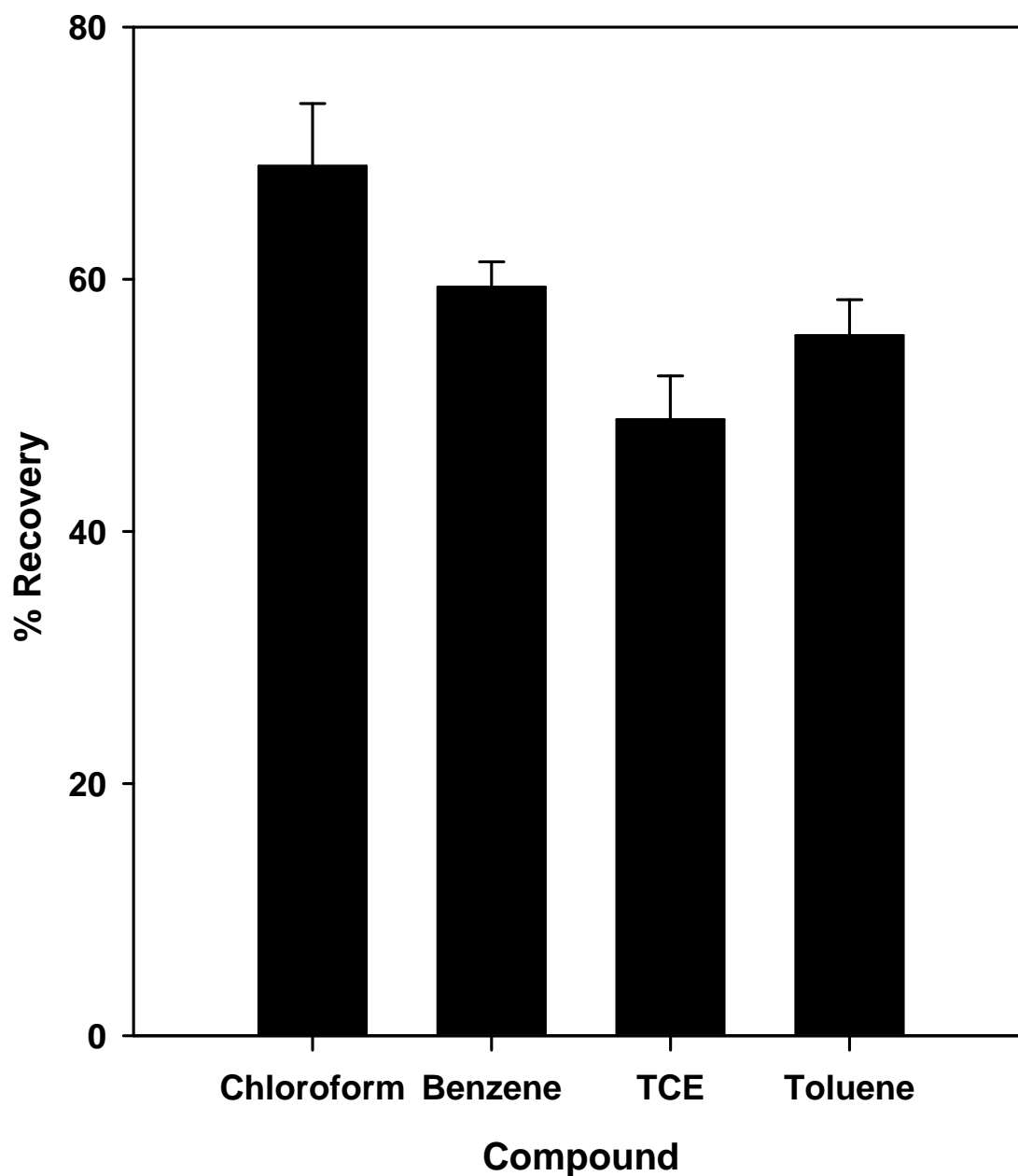


Figure 17. Summary of average VOC recoveries from Carboxen™ 569 (200 mg) for sorbent experiments using NTS Area 26 soil samples (5 g) with 5%, 10%, and 15% water content. The samples were stored at ambient temperature. The recoveries for the moisture levels were similar and the combined results are shown. VOC recoveries were in pyridine.

Solvent Extraction Comparison

As stated above, USEPA Method 5035A requires methanol extraction (preservation) for samples with high VOC concentrations prior to purge-and-trap analysis. At the time of this study, a working sparging apparatus was not available to compare recoveries by the USEPA SW-846 purge-and-trap analytical method to the SPME-GC/MS method. Solvent preservation was compared to Carboxen™ 569 sorbent preservation using the SPME-GC/MS method implemented in this study. Samples were prepared with NTS Area 26 soil (5 g) with soil moisture levels of 5% and 10% by weight. The soil samples were spiked with 7.42, 4.37, 7.32, and 4.33 µg of chloroform, benzene, TCE, and toluene, respectively, pickled in 5 mL of methanol, and stored for approximately 900 hours at room temperature. The samples were analyzed by the SPME-GC/MS method described previously. VOC recoveries for both moisture levels were similar and the results were combined. The VOC recoveries for these experiments are shown in Table 12 and Figure 18. The VOC recoveries for samples preserved in methanol were comparable to recoveries for samples preserved with Carboxen™ 569 sorbent, with the exception of Toluene, which was lower.

Table 12. Comparison of average VOC recoveries from methanol extraction and Carboxen™ 569 sorbent.

Analyte	Analyte Added (µg)	Methanol Extraction % Recovery	Carboxen™ 569 % Recovery
Chloroform	7.42	68.5 ± 14.9	69.0 ± 4.96
Benzene	4.37	53.1 ± 6.66	59.4 ± 2.01
TCE	7.32	45.0 ± 5.49	48.9 ± 3.47
Toluene	4.33	30.8 ± 3.12	55.5 ± 2.85

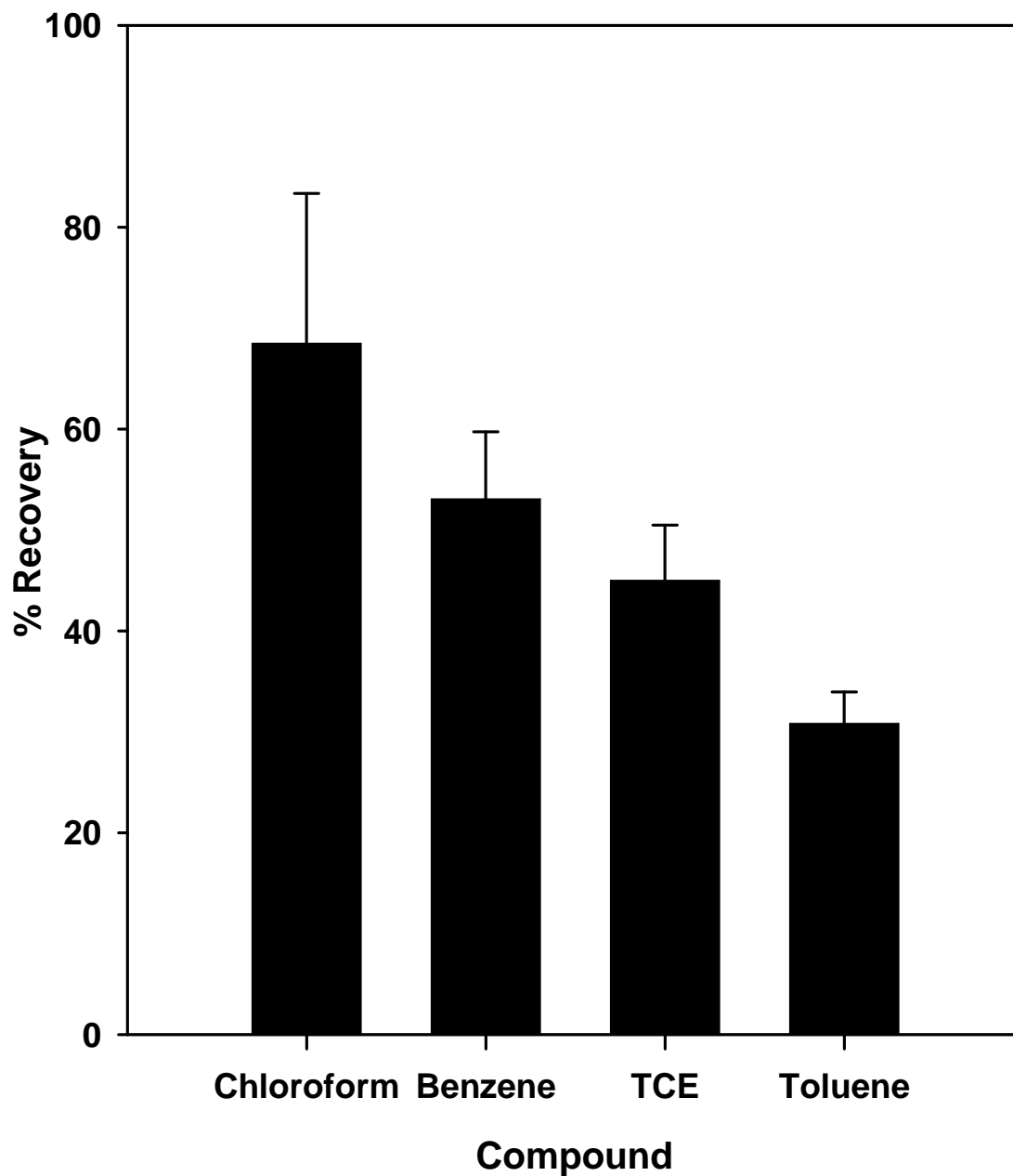


Figure 18. Summary of average VOC recoveries for methanol (5 mL) extraction (preservation) experiments using NTS Area 26 soil samples (5 g) with 5%, and 10% water content. The samples were stored at ambient temperature. The recoveries for the moisture levels were similar and the combined results are reported.

Characterization of Carboxen™ 569

Several experiments were performed to evaluate Carboxen™ 569 as a VOC sorbent under different conditions. These trials were conducted using the 40-mL modified VOA vials described previously (Figure 12). The soil used for these experiments was from NTS Area 26. All soil samples were 5 g and the same concentration of VOC standard solution was added to each sample (7.42, 4.37, 7.32, and 4.33 µg of chloroform, benzene, TCE, and toluene, respectively). The Carboxen™ 569 (200 mg) was added to the porous stainless-steel tube inside the modified VOA vial.

Effect of Sample Storage Temperature

The results for the effect of sample storage temperature are shown in Table 13 and Figure 19. Two sets of samples were prepared at 5% and 10% moisture levels and stored at -15 °C and ambient temperature (~22 °C). The storage time varied for each set of samples, but no significant differences in VOC recoveries were observed. The results indicate that storage temperatures did not have a great effect on VOC recoveries. Overall, recoveries with Carboxen™ 569 were slightly better from the samples stored at -15 °C compared to VOC recoveries from the samples stored at ambient temperature.

Table 13. Average VOC recoveries from Carboxen™ 569 for samples with 5% and 10% water content, stored at ambient temperature and -15 °C.

Compound	5% H ₂ O -15°	10% H ₂ O -15°	5% H ₂ O Ambient T	10% H ₂ O Ambient T
	% Recovery	% Recovery	% Recovery	% Recovery
Chloroform	60.0 ± 8.59	69.0 ± 4.96	60.8 ± 9.17	56.8 ± 8.94
Benzene	54.1 ± 9.73	59.4 ± 2.01	49.5 ± 6.40	46.4 ± 4.61
TCE	45.2 ± 8.31	48.9 ± 3.47	40.2 ± 6.59	40.7 ± 6.40
Toluene	61.3 ± 18.6	55.5 ± 2.85	46.9 ± 6.46	45.9 ± 9.71

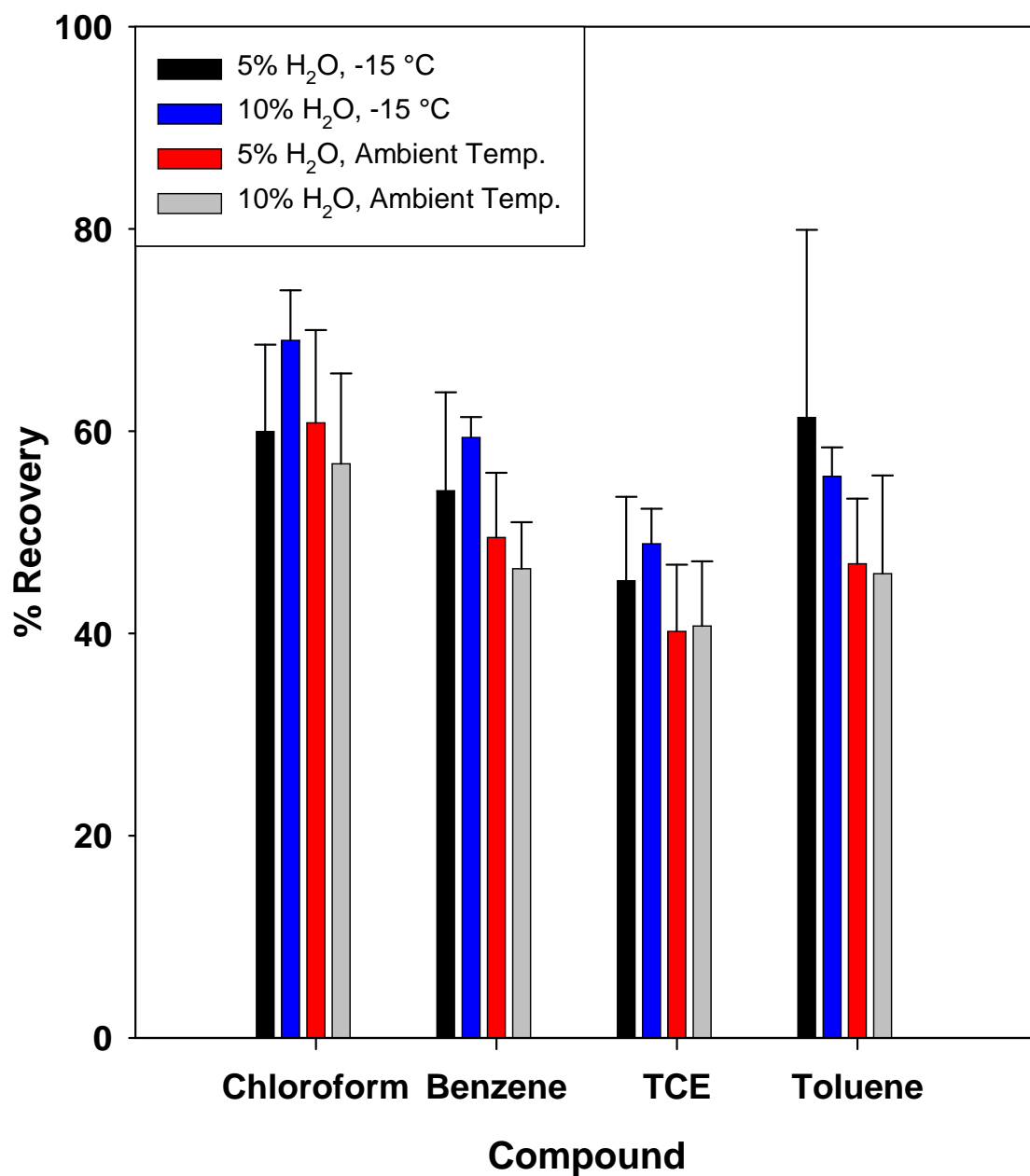


Figure 19. Summary of average VOC recoveries for NTS Area 26 soil samples (5 g) with 5% and 10% water content stored with CarboxenTM 569 (200 mg) at ambient temperature and at -15 °C. VOC recoveries were in pyridine.

Effect of Sample Storage Time

The results for the effect of sample storage time with Carboxen™ 569 are shown in Tables 14 and 15 and Figure 20. USEPA Method 5035A recommends sample preservation by freezing ($< -7^{\circ}\text{C}$) for long-term storage (14 days). Soil samples were prepared with 5% and 10% water content by weight, and stored from 50 to approximately 300 hours at -15°C before analysis. Benzene results were not reported for the 5% water content samples that were stored for 329 hours, because recoveries for these samples significantly exceeded 100%. The source of contamination or error was not determined. Prolonged storage does not have a great effect on VOC recovery. The results for samples with 10% water content were better than those with 5% water content.

Table 14. Average VOC recoveries from Carboxen™ 569 for long-term storage of samples with 5% water content, at -15°C .

Total Time Stored (h)	Chloroform % Recovery	Benzene % Recovery	TCE % Recovery	Toluene % Recovery
71.5	51.0 ± 2.05	36.7 ± 7.18	30.8 ± 4.99	33.2 ± 7.99
157.0	65.4 ± 8.82	56.6 ± 4.07	48.2 ± 0.74	77.2 ± 15.2
208.9	55.2 ± 5.03	45.2 ± 1.89	37.5 ± 1.96	41.1 ± 2.51
329.0	60.8 ± 9.49	—	51.5 ± 4.70	69.5 ± 13.5

Table 15. Average VOC recoveries from Carboxen™ 569 for long-term storage of samples with 10% water content, at -15°C .

Total Time Stored (h)	Chloroform % Recovery	Benzene % Recovery	TCE % Recovery	Toluene % Recovery
53.4	72.2 ± 5.13	59.7 ± 0.93	46.4 ± 0.94	61.3 ± 1.88
137.1	72.0 ± 9.01	59.7 ± 3.24	49.2 ± 0.99	58.2 ± 1.84
185.5	72.4 ± 1.14	59.4 ± 0.54	49.3 ± 6.93	56.1 ± 0.45
336.3	61.9 ± 1.14	62.1 ± 1.90	50.5 ± 3.90	55.6 ± 4.68

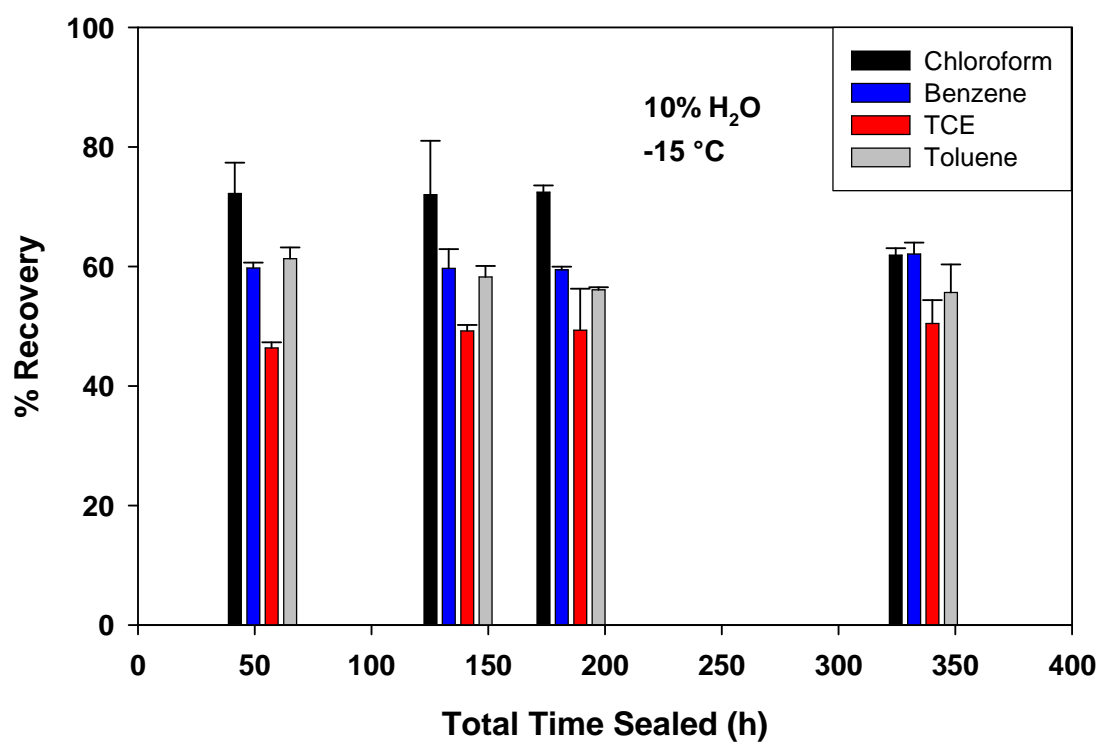
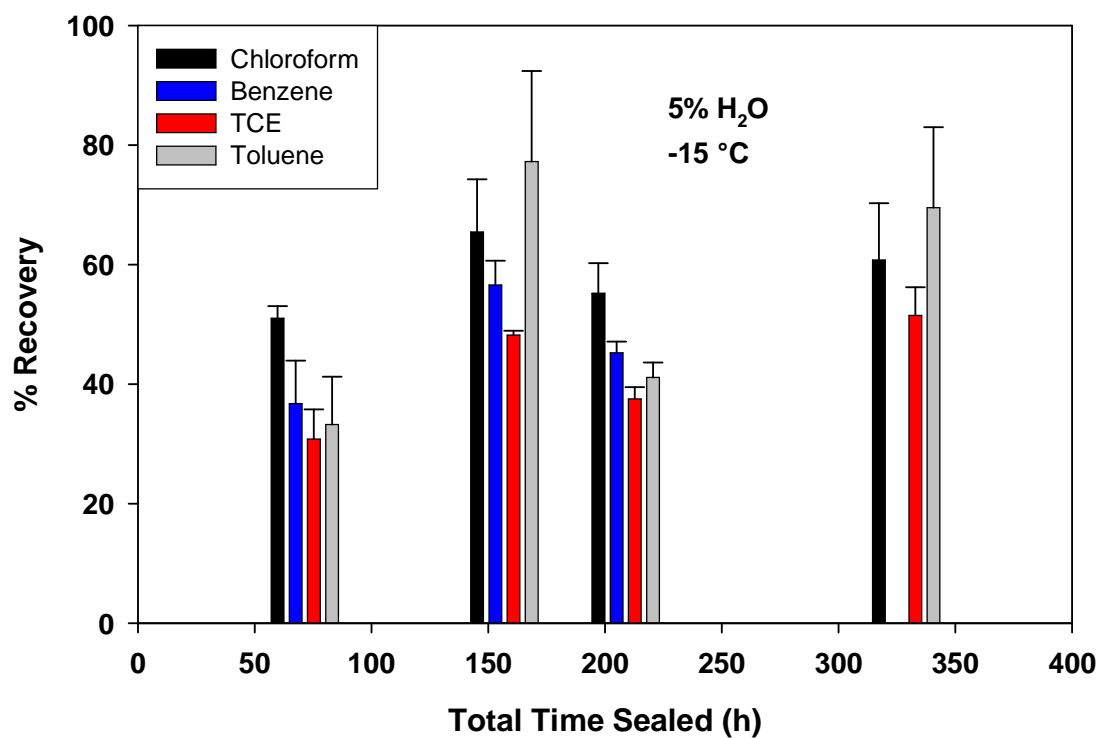


Figure 20. VOC recoveries presented as a function of sample storage time. NTS Area 26 soil samples (5 g) were stored in the Modified VOA Vial (40 mL) with Carboxen™ 569 (200 mg) at -15 °C with 5% and 10% water content. VOC recoveries were in pyridine.

VOC Recovery in Absence of Soil

Experiments were conducted to examine the recovery of VOCs from Carboxen™ 569 in VOA vials without soil samples. The average recoveries for these experiments were 10% to 20% higher than for recoveries of VOCs from Carboxen™ 569 in VOA vials with soil samples. The lower recoveries observed in the presence of soil (with the exception of chloroform) may indicate that some of the VOCs are being trapped in slow-desorption or “firmly-bound” sites. Table 16 and Figure 21 show Carboxen™ 569 recoveries of VOCs corrected for loss from empty vials. The loss mechanisms for VOCs preserved by Carboxen™ 569 in the absence of soil are not understood. Sample integrity may have been compromised by VOC diffusion through the vial septum, poor sealing of the vial, or incomplete VOC desorption from the resin.

Table 16. Average VOC recoveries from Carboxen™ 569 in vials without soil compared to VOC recoveries from empty vials (no soil or sorbent) and VOC recoveries with soil.

Analyte	Carboxen % Recovery (no soil)	Empty Vial % Recovery	Carboxen % Recovery (no soil) Corrected for VOC loss from Vial	Carboxen ¹ % Recovery (with soil)
Chloroform	67.9 ± 9.51	91.4 ± 10.9	74.3 ± 13.6	69.0 ± 4.96
Benzene	72.3 ± 10.8	91.4 ± 10.9	79.2 ± 15.1	59.4 ± 2.01
TCE	62.0 ± 12.6	82.8 ± 10.0	75.0 ± 17.7	48.9 ± 3.47
Toluene	76.7 ± 14.9	86.0 ± 10.4	89.2 ± 20.4	55.5 ± 2.85

¹Data from Table 11, Figure 17.

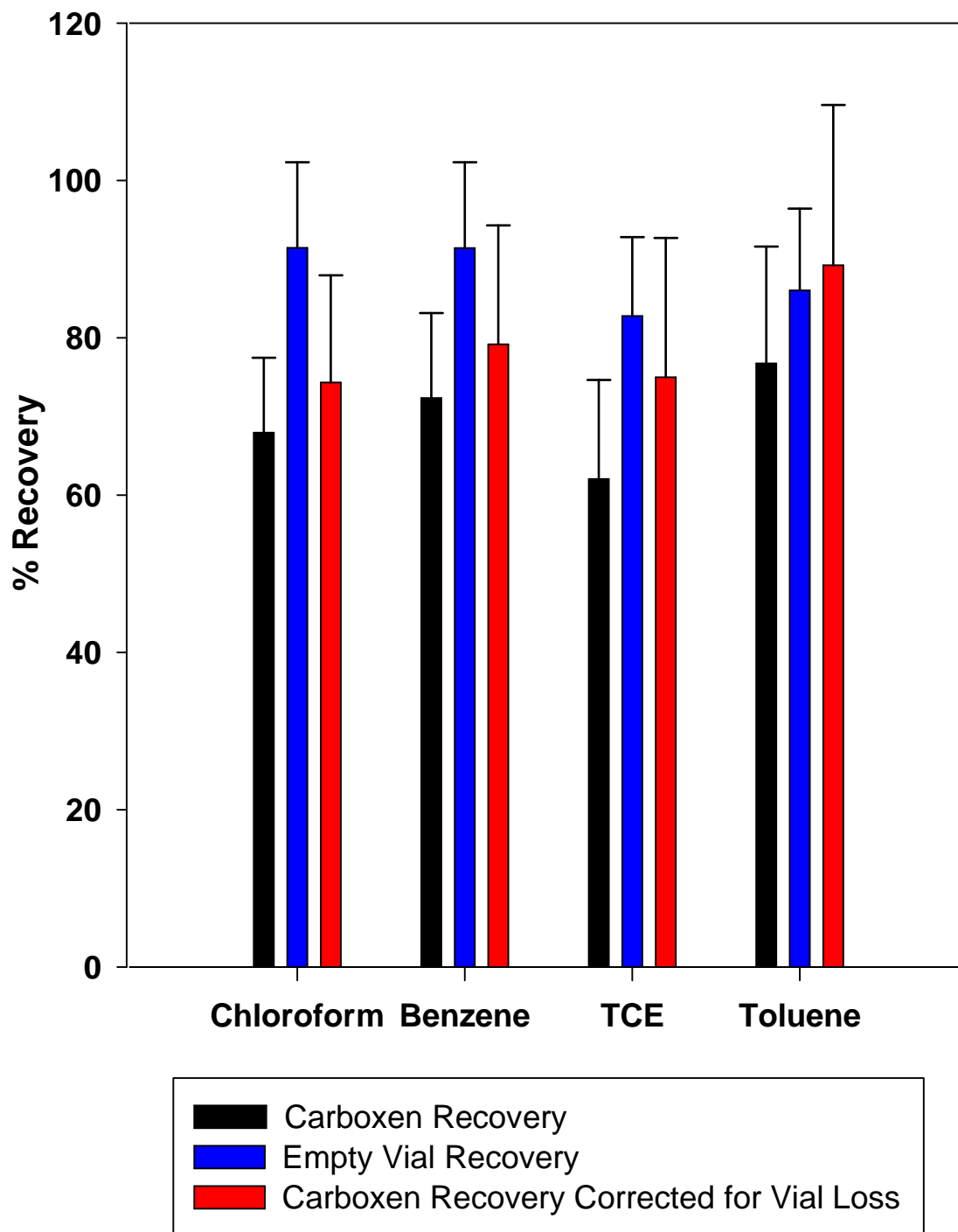


Figure 21. Summary of average VOC recoveries from Carboxen™ 569 (200 mg) in vials without soil compared to VOC recoveries from empty vials (no soil or sorbent). VOC recoveries from Carboxen™ 569 were in pyridine. VOCs recovered from empty vials were measured by headspace SPME-GC/MS analysis. The Carboxen™ 569 recoveries were corrected for VOC loss from the empty vial.

Kinetics of VOC Sequestration

While most preservation studies focus on the time between sampling and analysis, the Carboxen™ 569 VOC-sequestration method must also take into account the amount of time required for transfer of VOCs to the Carboxen™ phase. Sorption involves transfer of the target compound to the sorbent surface area and then a sequestration step that most likely involves diffusion through macropores, mesopores, and micropores. The kinetics of VOC sequestration was tested by adding a known quantity of VOCs (7.42, 4.37, 7.32, and 4.33 µg of chloroform, benzene, TCE, and toluene, respectively) to empty (no soil) 60-mL glass septum-sealed vials in the presence of Carboxen™ 569. The fraction of the individual VOC was then monitored as a function of exposure time using the SPME-GC/MS method. Near complete sequestration was achieved in ~5 hours for each of the four test compounds (Table 17) (Figure 22). To a first approximation, sorption of the VOCs onto the Carboxen™ 569 followed simple first order kinetics. The half-life for sorption onto the Carboxen™ 569 was ~0.4 hours. The analytes were completely transferred to the sorbent after ~10 hours of exposure time.

Table 17. Kinetics of VOC sequestration by Carboxen™ 569.

Sorption Time (h)	Chloroform % Vapor	Benzene % Vapor	TCE % Vapor	Toluene % Vapor
0.4	66.8	62.0	69.4	74.524
1	26.8	17.2	19.9	21.606
2	8.59	2.69	3.85	3.592
3	2.86	0.67	1.18	0.956
5	0.71	0.07	0.06	0.027
10	0.14	0.02	0.01	0.003
24	0.01	0.02	0	0.002

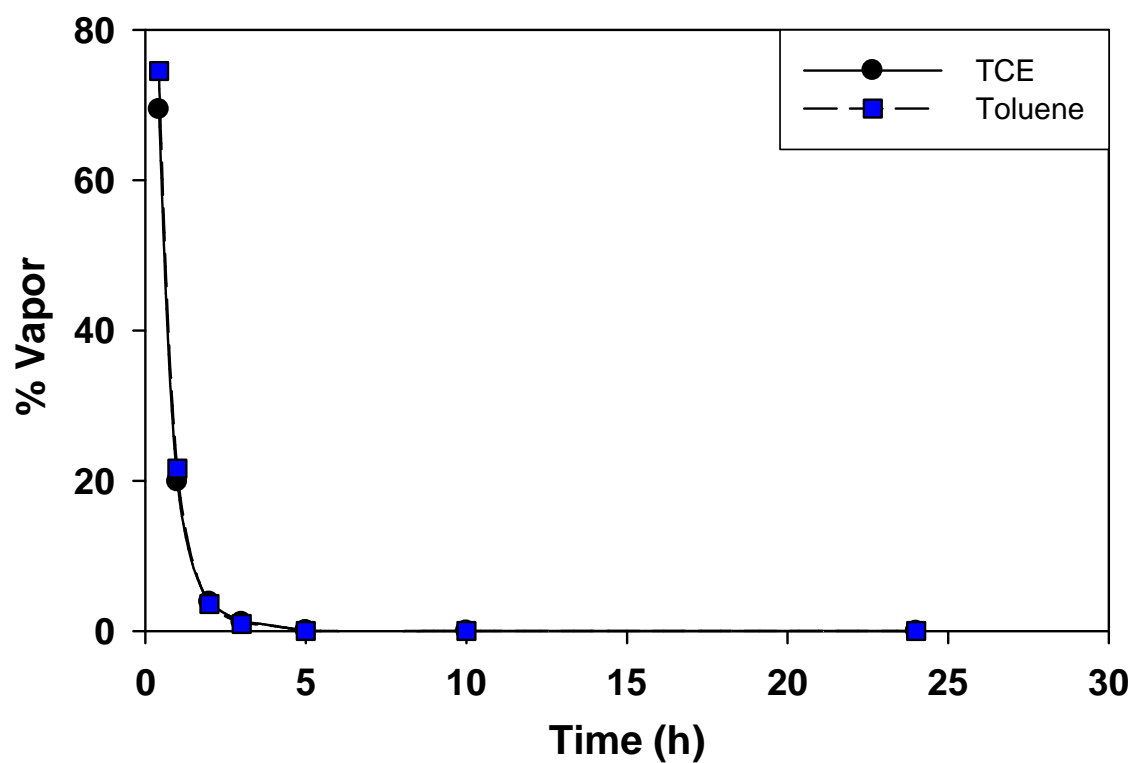
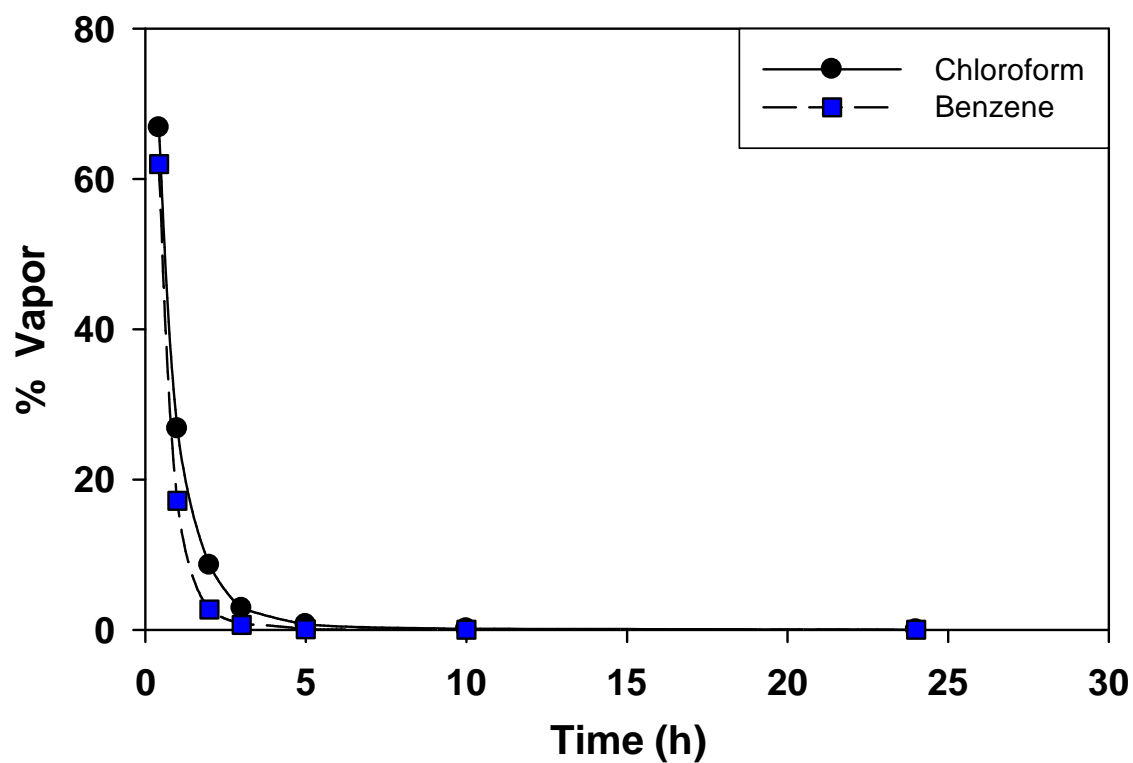


Figure 22. Kinetics of VOC sequestration by 200 mg of Carboxen™ 569 from a 60-mL septum-sealed vial. The half-life for sorption onto Carboxen™ 569 was ~0.4 hours.

Carboxen™ 569 Preservation Soil Study

The Carboxen™ 569 sample preservation method was evaluated with two other types of soils. A certified VOA contaminated soil sample was obtained from Resource Technology Corporation (RTC). RTC VOA soil contained 0.5% organic carbon with very little carbonate. The soil was a Sandy Loam; however, there was insufficient sample for a particle size analysis. As a sample with significantly different soil properties, Pahokee peat was obtained from the International Humic Substance Society (IHSS) (Athens Georgia). Pahokee peat is 45.70% organic carbon with no detectable carbonate. The calibration curves for the RTC soil and Pahokee peat samples were prepared from certified halocarbon and aromatic standards (100 µg/mL) obtained from Ultra Scientific. The same standards from Ultra Scientific were used to spike the Pahokee peat samples.

RTC VOA Soil

Six sample vials with VOA contaminated soil (5 g each) were received from RTC. The vendor prepared the samples 6 months in advance of certification. A 30-g sample was split into 6 samples - 5 g in each vial - inside a pressurized (argon gas) glove box (4 °C) at the time of shipment. The vendor estimates losses to be ~3% (personal communication with an RTC technician). Five of the samples were transferred to 5 larger vials to facilitate the Carboxen™ 569 VOC-preservation procedure. One of the 6 samples was preserved with 5 mL of methanol, no sorbent added. In order to minimize VOC loss during sample transfer, each of the 5 shipping vials containing the RTC soil was opened and then placed inside a larger vial along with a stainless-steel tube filled with 200 mg of Carboxen™ 569. The larger external vial was sealed with a Teflon®-lined septum. All samples were then stored for ~75 hours. The stainless-steel tubes filled with

sorbent were removed from the five Carboxen™ 569 preserved samples. The VOCs sequestered by the sorbent were recovered in pyridine. Five mL of methanol was added to each vial to extract the residual analytes from the soil. The 6 RTC VOA samples were analyzed by the SPME-GC/MS procedure. Figures 23 and 24 are representative chromatograms of RTC VOA soil analyzed by SPME-GC/MS.

The results for VOC recoveries from RTC VOA soil are in Table 18 and Figures 25 and 26. The combined analyte recoveries from RTC soil are comparable to the range of recoveries reported for the Prediction Interval on the certificate of analysis (Appendix I) for the samples (Tables 18 and 19). The recoveries of VOCs from the Carboxen™ 569 sorbent were combined with the recoveries of VOCs extracted from the soil after the Carboxen™ 569 was removed from the sample vial. The VOC recoveries from the soil were in methanol. Combined benzene and toluene fractions (Table 18) are within the reported RTC Confidence Interval (Table 19) (Appendix I). The combined recoveries for all VOCs (Table 18) fall within the Prediction Interval (Table 19) (Appendix I). Lower recoveries of target analytes in the samples compared to the certified values may be explained by the soil sample preparation and treatment before analysis or by the conversion of the VOCs to a firmly-bound fraction during sample storage.

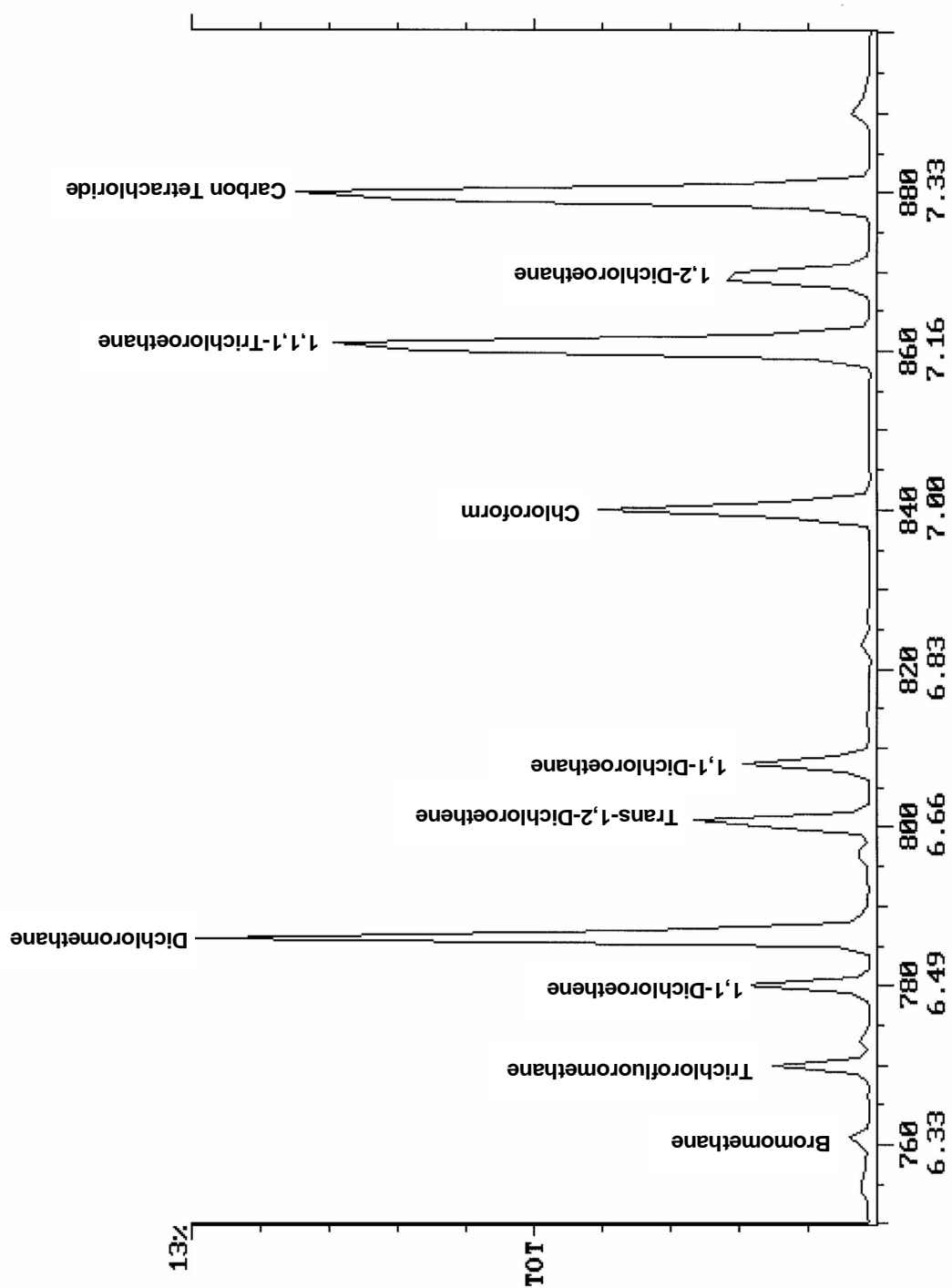


Figure 23. Representative chromatogram of halocarbon-spiked RTC VOA soil analyzed by SPME-GC/MS.

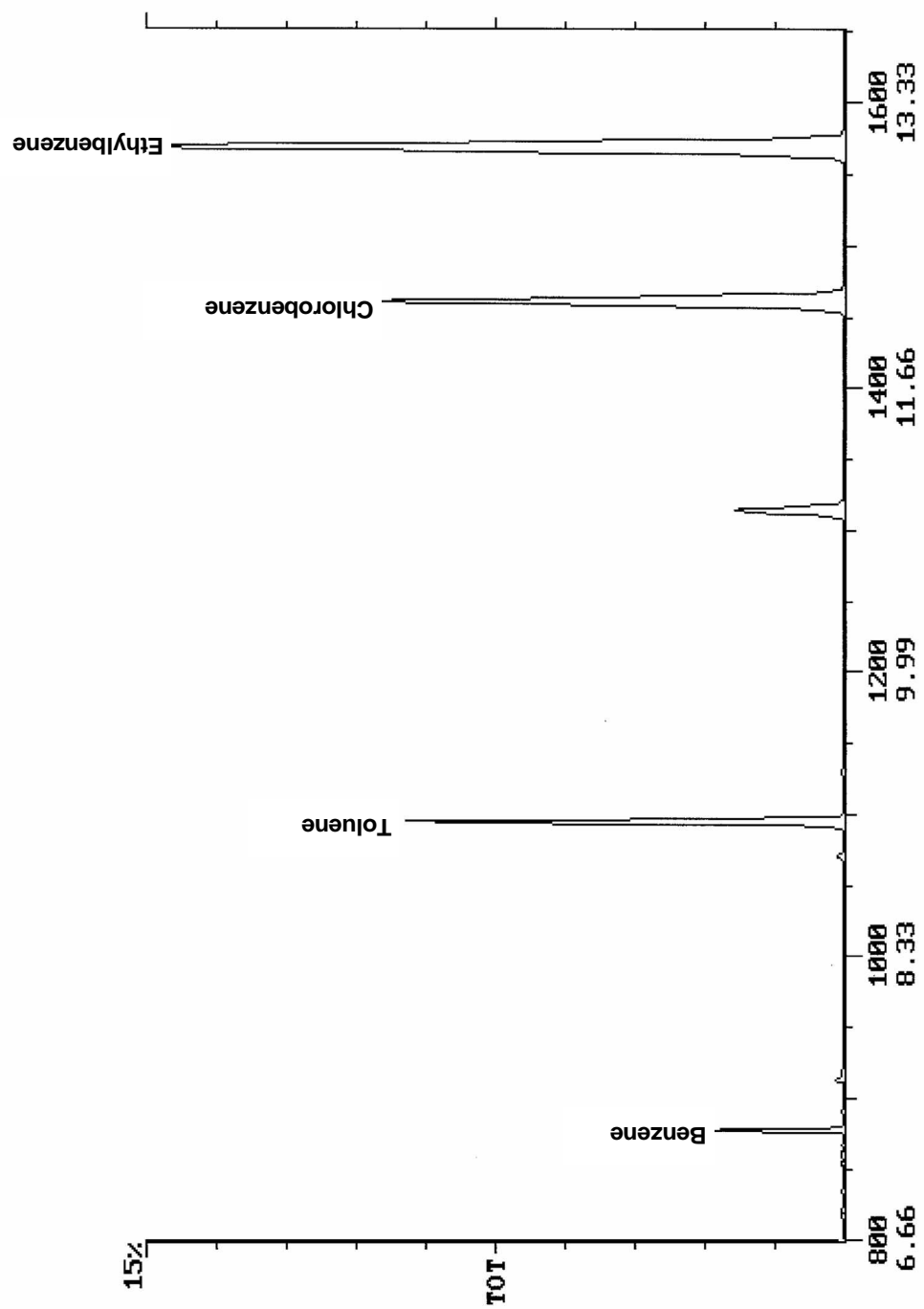


Figure 24. Representative chromatogram of aromatic-spiked RTC VOA soil analyzed by SPME-GC/MS.

Table 18. Average VOC recoveries from RTC VOA soil with SPME-GC/MS analysis.

Analyte	Carboxen Recovery ($\mu\text{g/kg}$)	Soil¹ Methanol Extraction ($\mu\text{g/kg}$)	Carboxen + Soil Methanol Extraction ($\mu\text{g/kg}$)	Soil² Methanol Extraction (No sorbent) ($\mu\text{g/kg}$)
Chloroform	44.2 \pm 4.45	32.9 \pm 4.27	77.1 \pm 8.72	98.9
Benzene	70.3 \pm 9.43	15.9 \pm 4.80	86.2 \pm 14.2	108.8
TCE	67.1 \pm 9.46	7.27 \pm 2.32	74.4 \pm 11.8	72.1
Toluene	189.8 \pm 24.40	11.9 \pm 4.42	201.7 \pm 28.81	186.5

¹Soil was preserved with Carboxen™ 569

²Soil was preserved in 5 mL of methanol; only one sample available for analysis

Table 19. RTC VOA soil certified analyte concentrations (Appendix I).

Analyte	RTC Reference Value¹ ($\mu\text{g/kg}$)	Confidence Interval ($\mu\text{g/kg}$)	Prediction Interval ($\mu\text{g/kg}$)
Chloroform	111 \pm 18.4	102 - 120	71.0 - 151
Benzene	107 \pm 22.3	97.1 - 116	58.9 - 154
TCE	117 \pm 15.0	110 - 124	84.7 - 150
Toluene	202 \pm 27.4	188 - 215	143 - 261

¹Determined by USEPA SW-846 Method 8260B: Volatile Organic Compounds by Gas Chromatography/Mass Spectrometry (GC/MS)

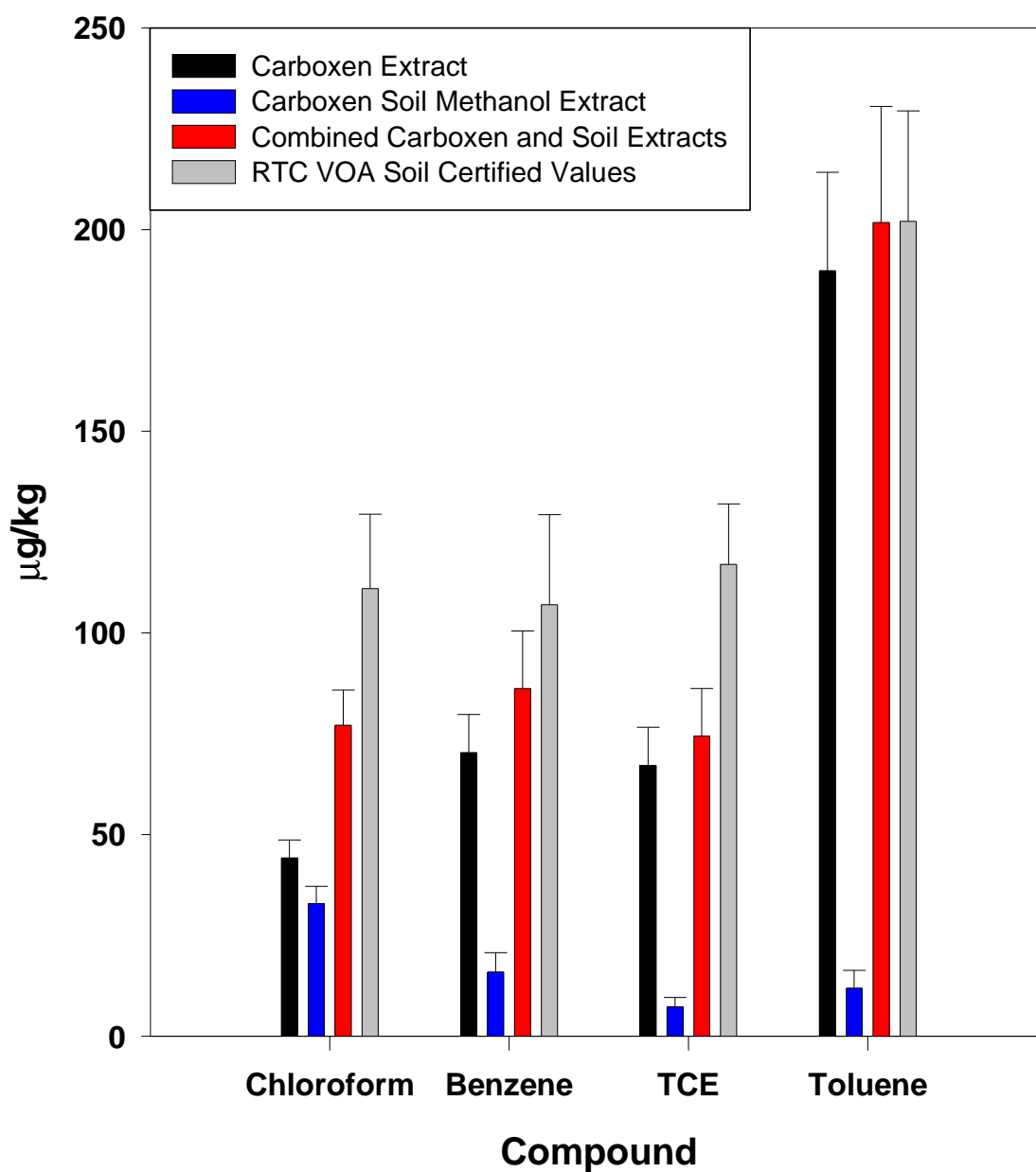


Figure 25. Summary of average VOC recoveries from RTC VOA soil with SPME-GC/MS analysis compared to RTC VOA soil certified values.

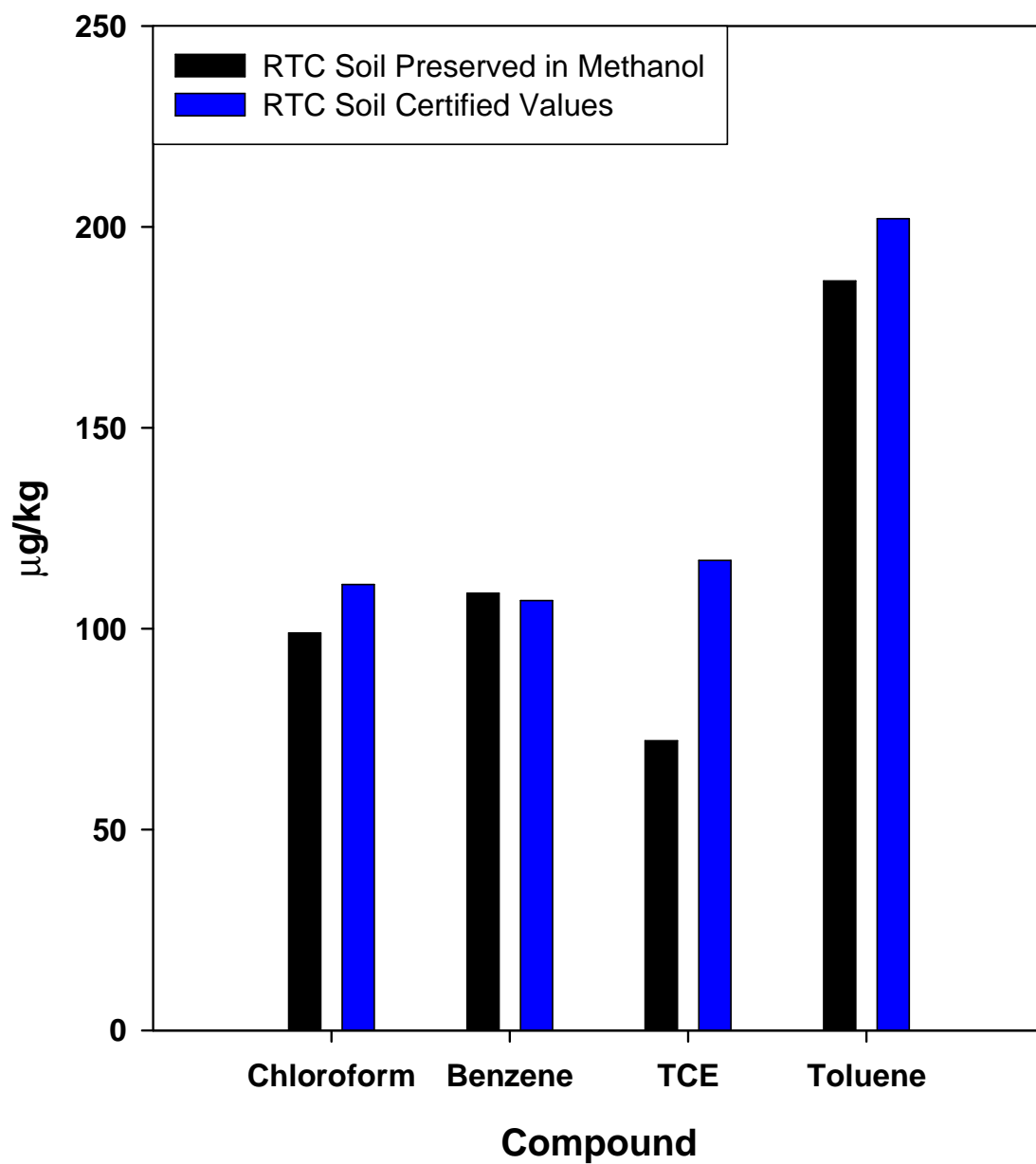


Figure 26. VOC recoveries from RTC VOA soil preserved in methanol compared to RTC VOA soil certified values.

Pahokee peat

In general, the average recoveries of VOCs from laboratory-spiked Pahokee peat samples by sorption onto Carboxen™ 569 were higher than for the average VOC recoveries from experiments performed with laboratory-spiked NTS Area 26 soil samples and the certified RTC VOA soil samples, with the exception of TCE (Table 20) (Figure 25). Statistically, TCE recovery was comparable to the average recoveries of TCE from RTC and Area 26 soil samples. The surface area (SA) of NTS Area 26 soil is greater ($14.2 \text{ m}^2/\text{g}$) than the SA for RTC VOA soil ($9.62 \text{ m}^2/\text{g}$) and the SA for Pahokee peat ($0.866 \text{ m}^2/\text{g}$), but the percent organic carbon is much higher for Pahokee peat (45.70%). The soils in this study with lower amounts of organic carbon and higher surface areas (Area 26 and RTC soil) may have had lower VOC recoveries because of mineral adsorption of the target analytes and their transfer to sorption sites in the soil matrix and subsequent conversion to a firmly-bound fraction during sample storage. The higher average VOC recoveries by Pahokee peat may be because of the soil's high organic carbon content. It has been reported that the soil organic matter of Pahokee peat's amorphous humic structure acts as a partition or "solvent-like" medium rather than as an adsorbent for the uptake of organic molecules (Chiou et al., 1990). This characteristic of Pahokee peat may allow for a greater probability of reversible sorption and a more readily available fraction of extractable analytes.

The results from the Carboxen™ 569 preservation soil study are shown in Tables 18 and 20 and Figures 25 and 27. The average recovery of chloroform from RTC VOA soil by sorption onto Carboxen™ 569 was lower (40%) and the recovery of toluene was higher (94%) than recoveries for chloroform (69%) and toluene (56%) from NTS Area 26

soil samples used in this study. Benzene (66%) and TCE (57%) average recoveries were higher for RTC soil than for NTS Area 26 soil (59% and 49%, respectively).

Table 20. Soil comparison of average VOC recoveries from Carboxen™ 569.

Analyte	RTC VOA Soil % Recovery	Pahokee peat % Recovery	NTS Area 26 Soil % Recovery
Chloroform	39.8 ± 4.00	101.9 ± 21.5	69.0 ± 4.96
Benzene	65.7 ± 8.81	93.9 ± 12.5	59.4 ± 2.01
TCE	57.4 ± 8.08	47.4 ± 15.2	48.9 ± 3.47
Toluene	94.0 ± 12.1	87.1 ± 8.63	55.5 ± 2.85

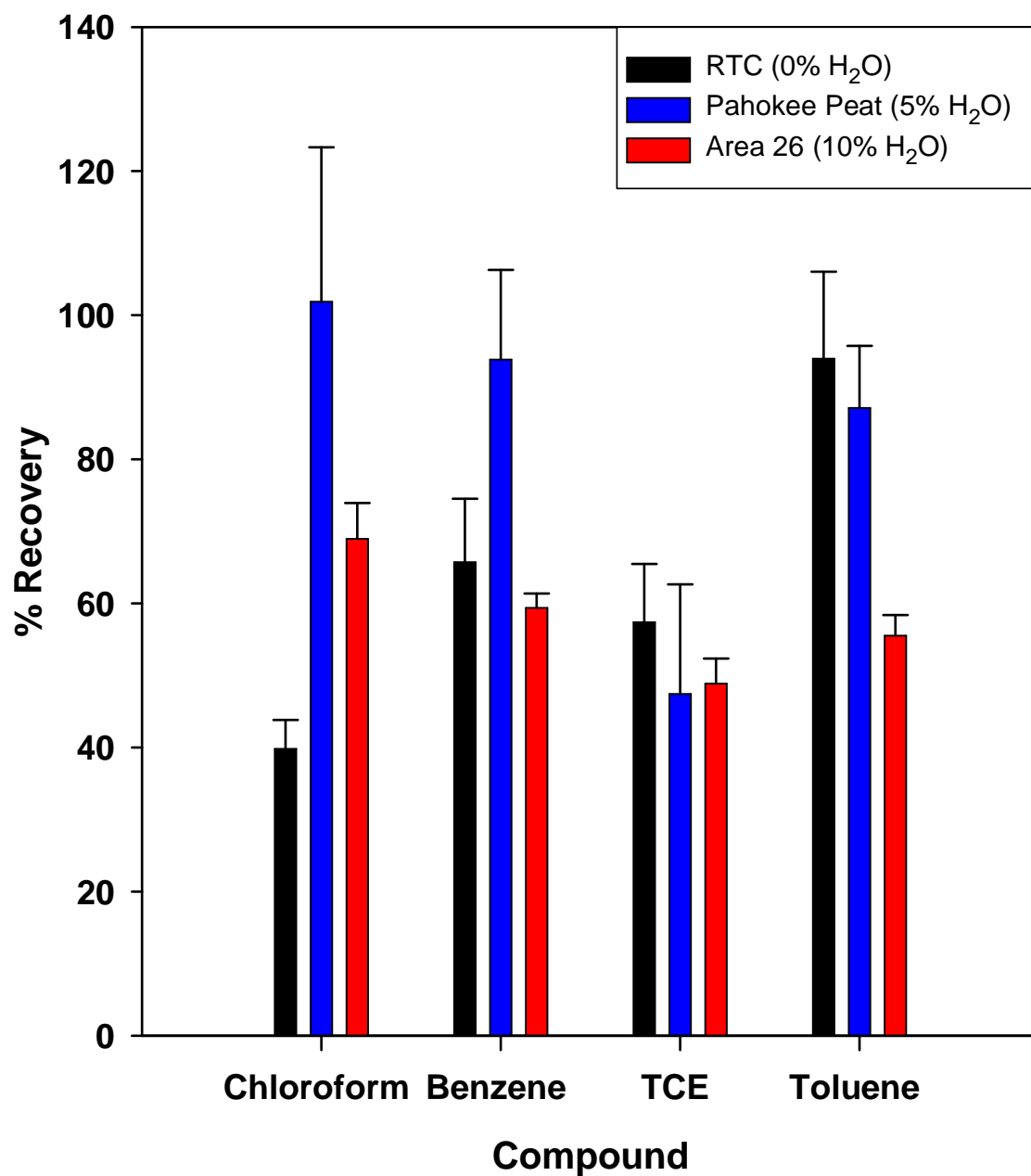


Figure 27. Soil comparison of average VOC recoveries from Carboxen™ 569 (200 mg). VOC recoveries were in pyridine.

CHAPTER 4

SLOW DESORPTION OF VOCs FROM SOIL

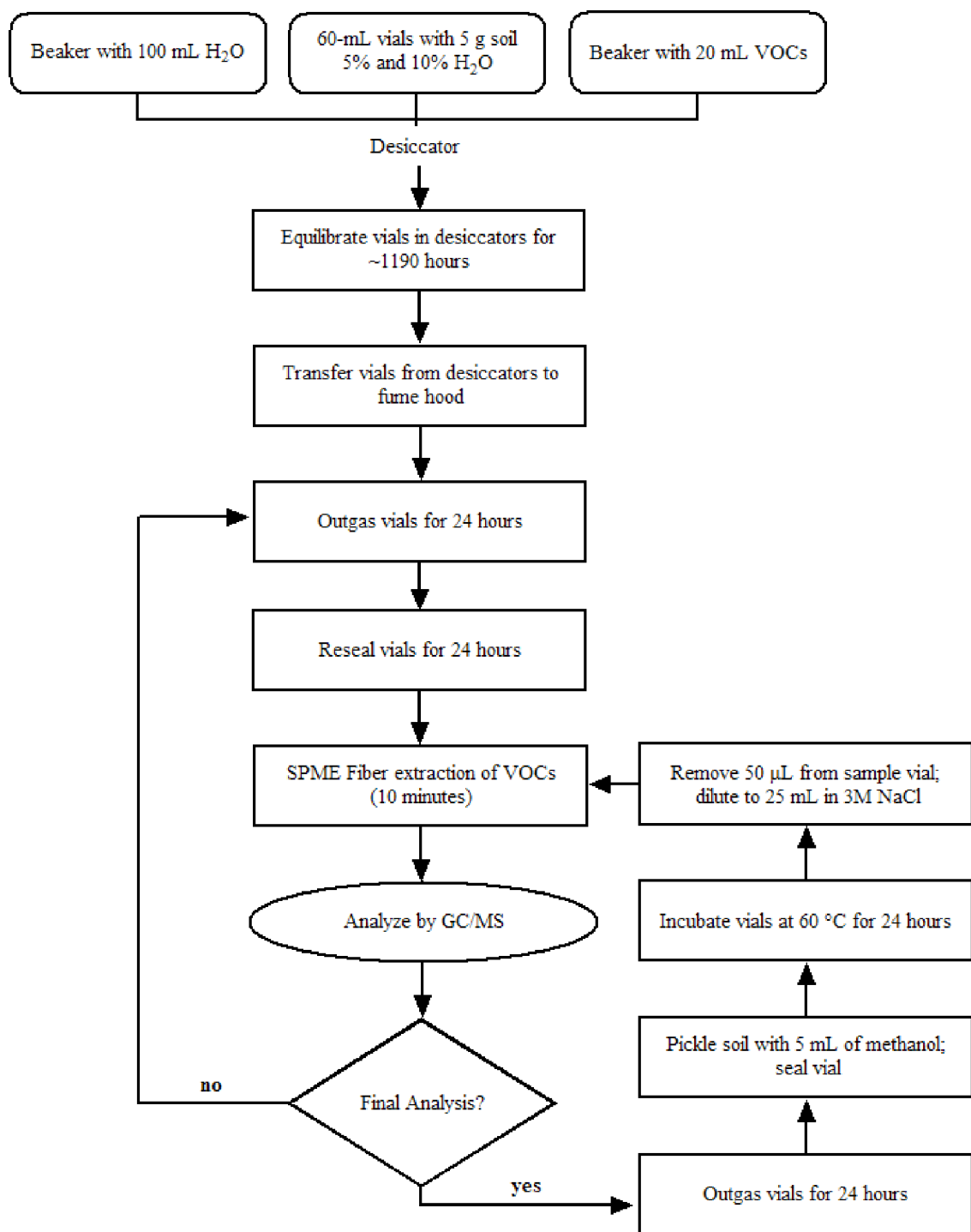
The lower VOC recoveries observed in the presence of soil may indicate that some of the contaminants are not easily desorbed. There is evidence that VOCs are being trapped in slow-desorption or “firmly-bound” sites of the soil. Steinberg et al., (1987) and Pignatello (1990a,b) found that several VOCs may become trapped in soil micropores or slowly diffuse through narrow pores. Pignatello and Xing (1996) have suggested an initial rapid release of a readily accessible labile fraction followed by prolonged desorption or slow release of a non-labile fraction. This slowly-desorbing or firmly-bound non-labile fraction may dominate under some circumstances and have important implications for proposed sampling, sample preservation, and analytical method. Experiments were carried out to investigate VOC entrapment in the soil micropores. The kinetics of VOC desorption was explored.

Formation of Residual Slow-Release VOC Fraction

Ten Las Vegas soil samples (5 g) were prepared in 60-mL headspace vials. The samples were divided into two sets of five each, one prepared with 5% moisture levels and the other with 10% moisture levels. Each set of samples was placed in a desiccator along with a beaker containing 100 mL of water and another beaker with 20 mL of VOCs (5 mL each of chloroform, benzene, TCE, and toluene). The beaker of water was to maintain the humidity at 100% to keep the soil samples from drying out. The VOC exposure to the samples was through the vapor phase only. The samples were allowed to equilibrate in the desiccators for approximately 1190 hours. Both sets of samples were

removed from the desiccators at the same time, placed inside the fume hood, and allowed to evaporate for 24 hours. Following evaporation, the sample vials were crimp-sealed and the soil was allowed to equilibrate for 24 hours. After sample equilibration, the vapor phase was analyzed by the SPME-GC/MS procedure described previously. After analysis, the seals were removed and the open vials were returned to the fume hood to evaporate again. After 24 hours, the vials were resealed, the samples allowed to equilibrate for 24 hours, and the vapor phase then analyzed by SPME-GC/MS. This procedure was repeated for all samples for multiple runs. After the final run, the samples were allowed to evaporate for 24 hours in the fume hood and then 5 mL of methanol was added to each vial to extract the residual VOCs from the soil. The vials were sealed and placed in the oven at 60 °C for 24 hours. After heating, the samples were removed from the oven and 1 mL of the methanol extract was transferred to a 2-mL screw-cap vial. The samples were analyzed by the SPME-GC/MS procedure (Schematic 2).

These experiments addressed the formation of a residual slow-release or firmly-bound fraction of VOCs in soil. The results in Tables 21 and 22 and Figures 28 and 29 show a firmly-bound VOC fraction forms after the soil is exposed to the VOCs in the vapor phase for an extended period of time (~1190 hours). There was an initial fast desorption of the labile fraction of sorbed VOCs followed by the slow desorption of a non-labile fraction. The recoveries of residual VOCs from methanol extractions of Las Vegas soil samples after extended desorption time by evaporation (~863 hours) are shown in Table 23 and Figure 30. The formation of a residual slow-release VOC fraction indicates partitioning of the compounds into and slow diffusion out of the soil particle pores, as well as VOC entrapment in particle micropores.



Schematic 3. Procedure to examine formation of residual slow-release fraction of VOCs in soil.

Table 21. Formation of a residual slow-release VOC fraction (5% water).

Total Time Open (h)	Chloroform (ng/gh)	Benzene (ng/gh)	TCE (ng/gh)	Toluene (ng/gh)
50.9	1.330	0.673	0.902	0.161
99.0	0.629	0.289	0.399	0.058
147.5	0.135	0.058	0.066	0.009
362.5	0.261	0.115	0.153	0.024
413.3	0.149	0.075	0.073	0.009
463.7	0.090	0.043	0.046	0.005
530.9	0.061	0.028	0.028	0.003
626.7	0.076	0.034	0.036	0.004
675.1	0.049	0.033	0.023	0.003
799.0	0.060	0.034	0.029	0.005
845.4	0.155	0.091	0.078	0.011

Table 22. Formation of a residual slow-release VOC fraction (10% water).

Total Time Open (h)	Chloroform (ng/gh)	Benzene (ng/gh)	TCE (ng/gh)	Toluene (ng/gh)
100.1	0.617	2.217	11.623	4.753
148.4	0.117	0.155	0.746	0.129
363.3	0.246	0.274	1.303	0.371
414.9	0.100	0.092	0.258	0.028
464.7	0.077	0.071	0.151	0.014
532.2	0.052	0.036	0.095	0.007
627.8	0.068	0.041	0.113	0.010
676.7	0.054	0.038	0.059	0.004
799.8	0.020	0.013	0.031	0.004
847.6	0.174	0.148	0.380	0.051

Table 23. Recoveries of residual VOCs from methanol extractions.

% Water	Chloroform (ng/g)	Benzene (ng/g)	TCE (ng/g)	Toluene (ng/g)
5	881.2	1084.4	1088.1	1074.1
10	850.5	1450.8	1332.5	1339.4

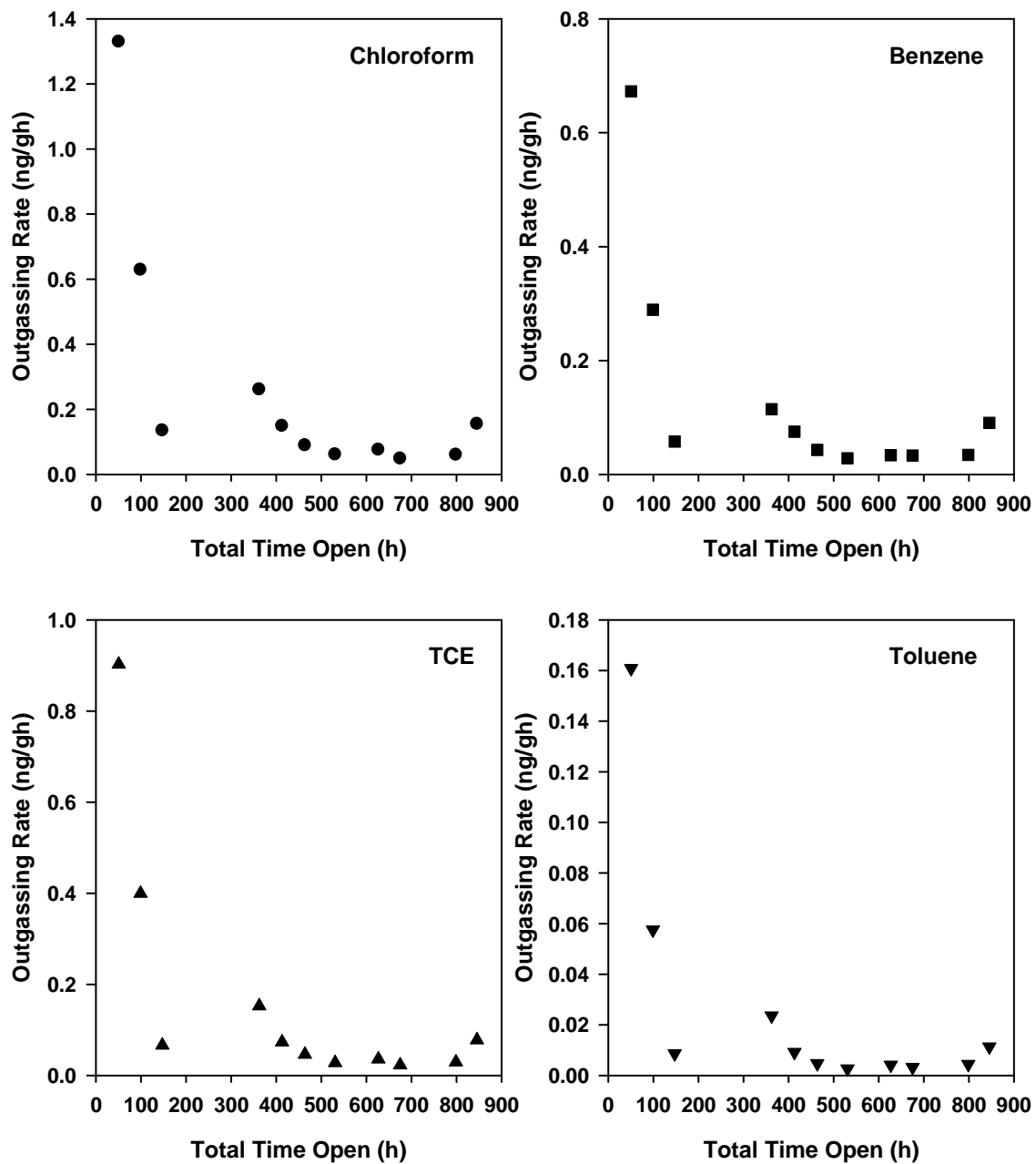


Figure 28. Formation of a residual slow-release VOC fraction in Las Vegas soil samples (5 g, 5% water content, and ambient temperature) after prolonged vapor-phase exposure (~1190 hours).

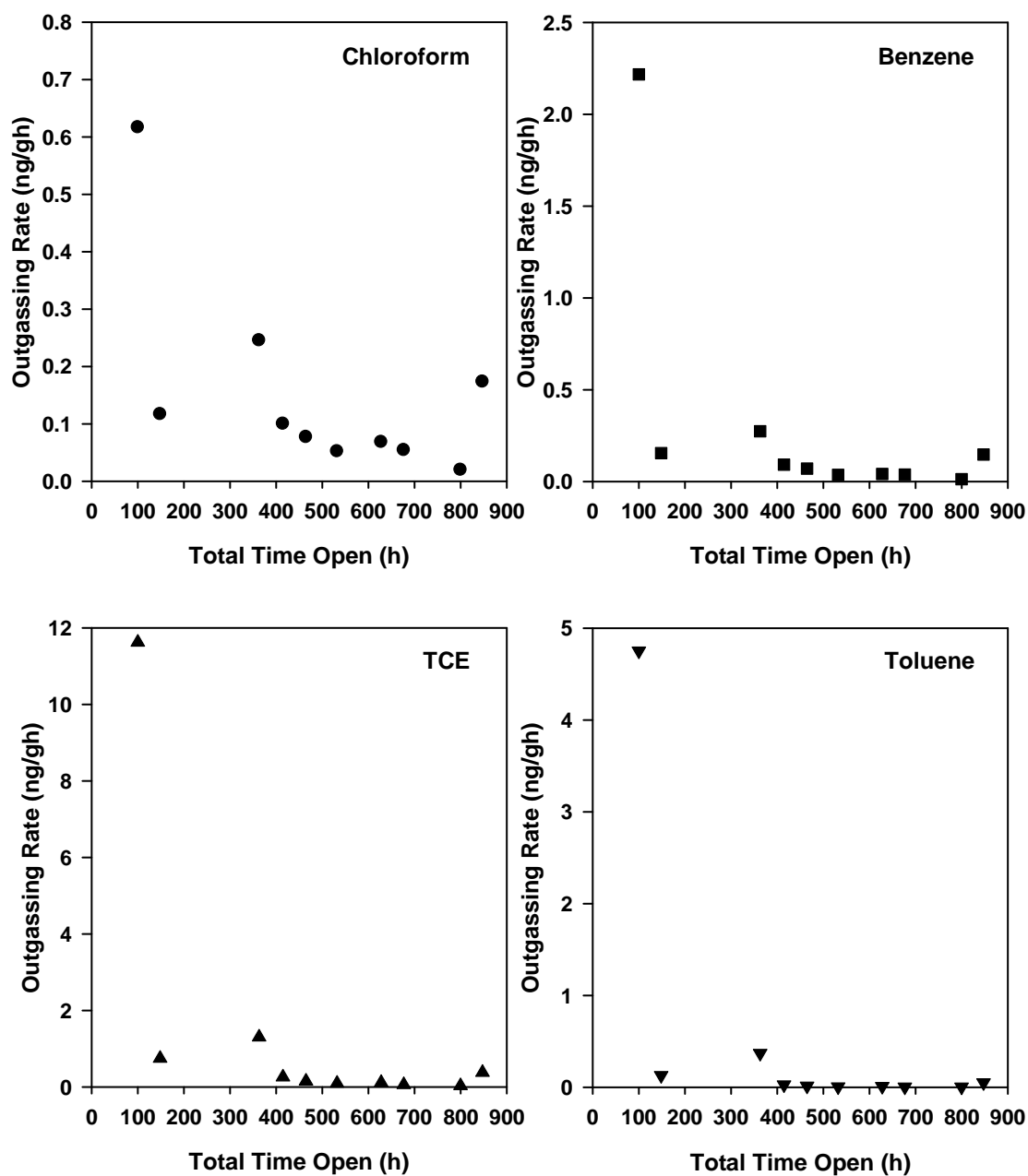


Figure 29. Formation of a residual slow-release VOC fraction in Las Vegas soil samples (5 g, 10% water content, and ambient temperature) after prolonged vapor-phase exposure (~1190 hours).

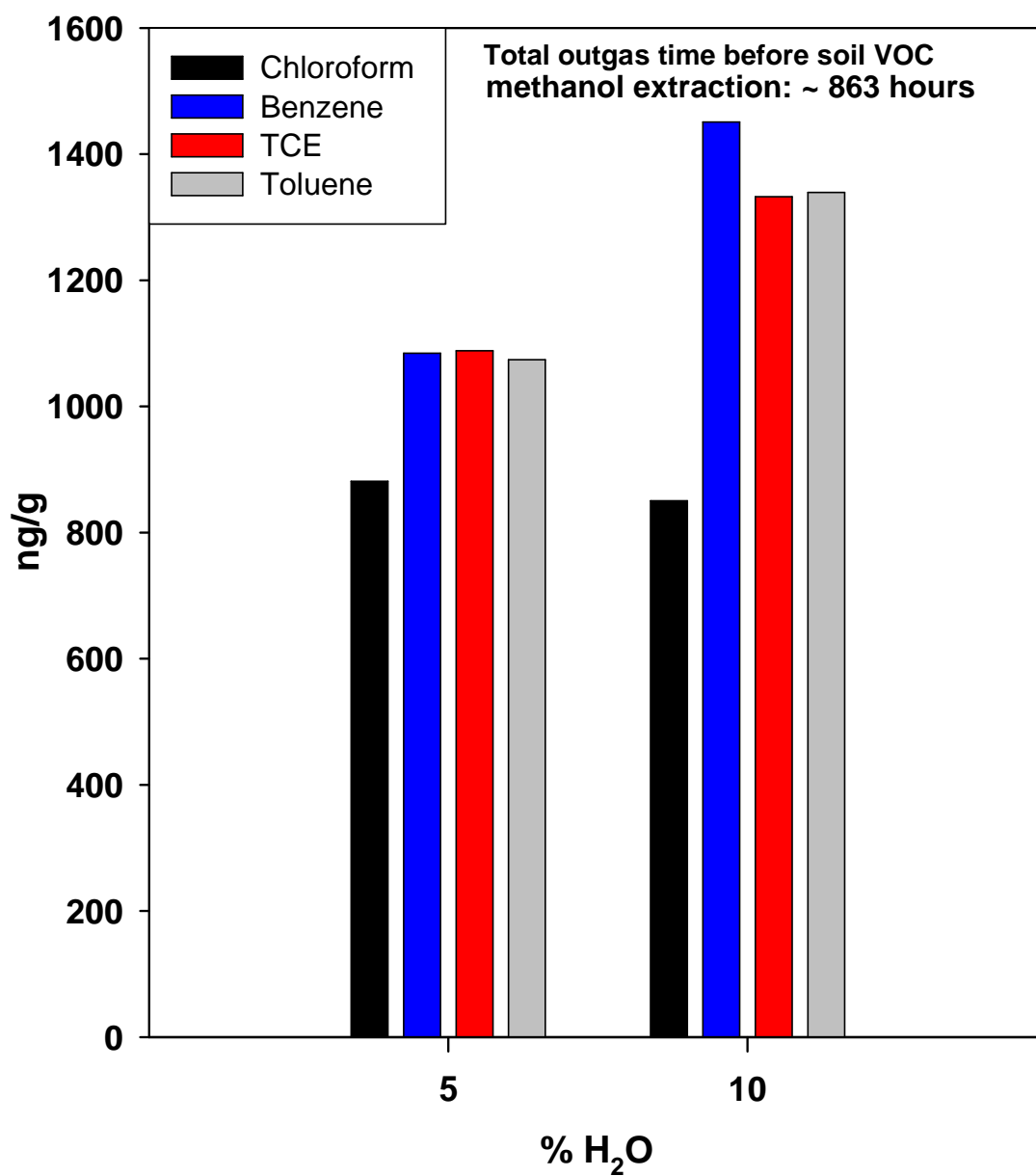
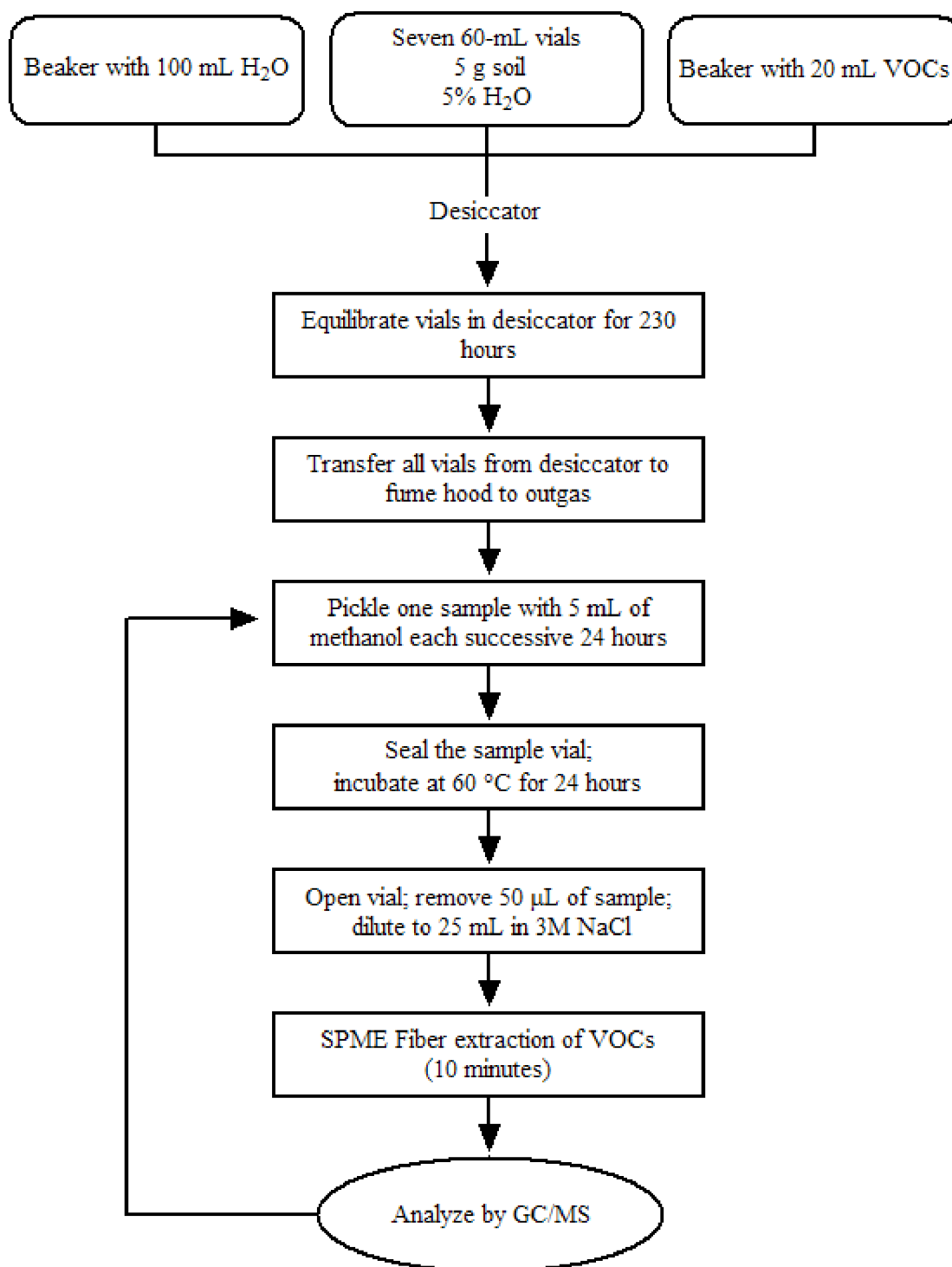


Figure 30. Recoveries of residual VOCs in methanol extractions of Las Vegas soil samples (5 g, 5% and 10% water content, and ambient temperature) after prolonged vapor-phase exposure (~1190 hours). Total outgas time for the soil samples before VOC methanol extraction was ~863 hours.

VOC Desorption Kinetics

Las Vegas soil samples were prepared in replicate in 60-mL headspace vials with 5 g of soil each and 5% moisture levels. The samples were placed in a desiccator along with a beaker containing 100 mL of water, to maintain the humidity, and another beaker with 20 mL of VOCs (5 mL each of chloroform, benzene, TCE, and toluene). The VOC exposure to the samples was through the vapor phase only. The samples were allowed to equilibrate in the desiccator for 230 hours at room temperature and then transferred to the fume hood to evaporate. One vial was removed from the fume hood every 24 hours and 5 mL of methanol added to extract the sorbed VOCs from the soil. The sample vial was sealed and then incubated at 60 °C for 24 hours. After heating, the sample was removed from the oven and 1 mL of the methanol extract was transferred to a 2-mL screw-cap vial. The sample was then analyzed by the SPME-GC/MS method. This procedure was repeated for each sample (Schematic 3).

This experiment was to determine the kinetics of the loss of the fast equilibrating (labile) VOC fraction versus the slowly-desorbing or firmly-bound fraction (non-labile). Table 24 and Figure 31 show that after the soil is exposed to the VOCs in the vapor phase for an extended period of time (~230 hours), the concentration of the remaining VOCs changes very little after the initial 24-hour desorption period. The data demonstrate the formation of a slowly-equilibrating VOC fraction.



Schematic 3. Procedure to determine desorption kinetics of VOCs in soil.

Table 24. Desorption kinetics of VOCs in soil.

Total Time Open (h)	Chloroform (ng/g)	Benzene (ng/g)	TCE (ng/g)	Toluene (ng/g)
24.2	2336.9	5057.8	4178.1	2530.0
48.2	2375.9	5250.0	3650.3	2226.2
72.6	2884.0	6408.4	3482.7	2898.9
96.9	2979.8	8033.6	3750.6	3384.0
120.5	2364.1	4897.9	3907.1	2053.1
144.6	2945.7	6955.9	5623.1	2892.4
168.9	1271.8	2516.7	2408.6	1250.9

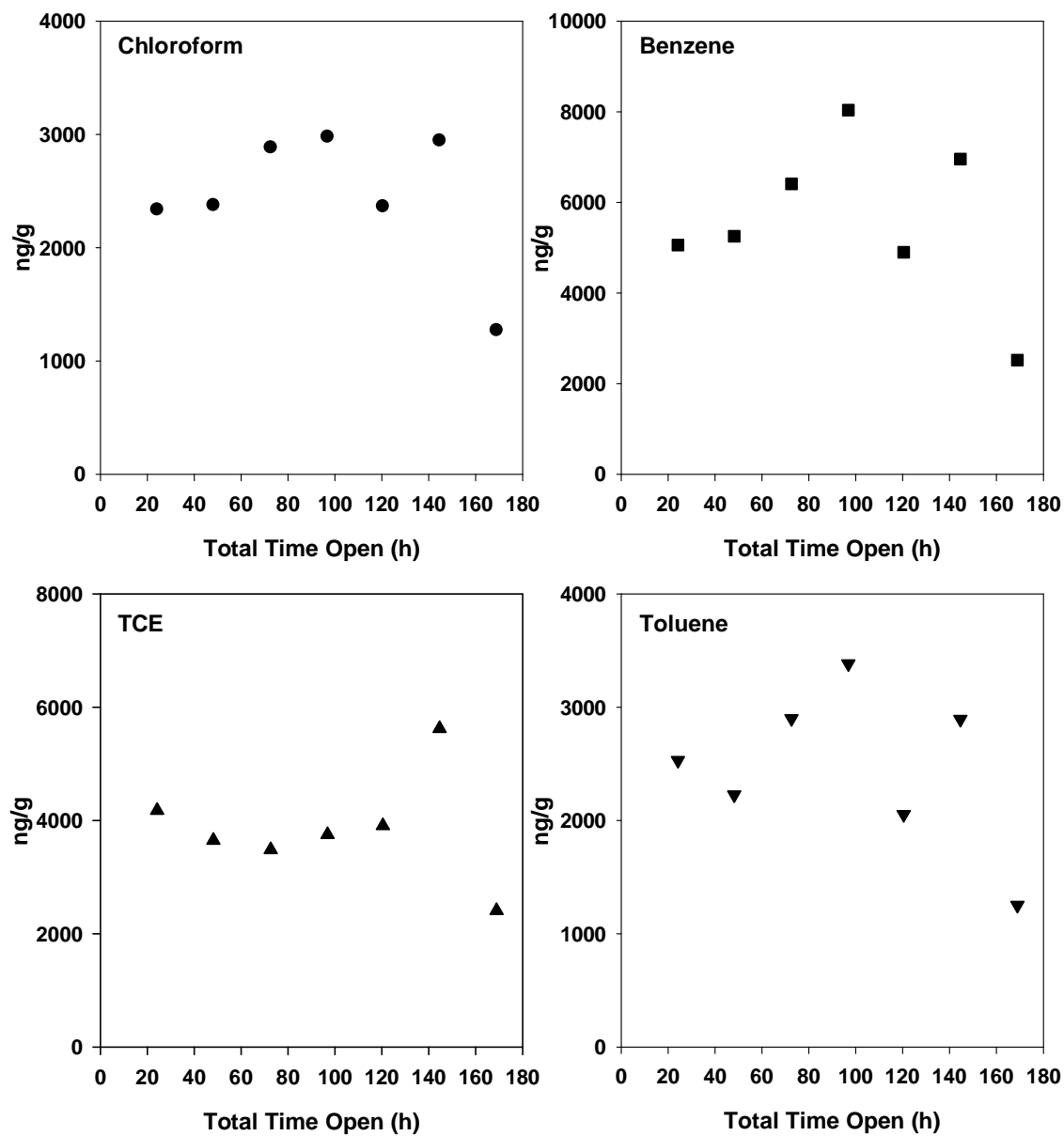


Figure 31. Desorption kinetics of VOCs in Las Vegas soil samples (5 g, 5% water content) after prolonged vapor-phase exposure (~230 hours at ambient temperature).

CHAPTER 5

CONCLUSIONS

In this study, a simple approach to sample preservation using solid-phase sorbents and commercially available materials was explored. With the modified VOA vial, the method should be straightforward to implement in the field. The analytical method used was based on solvent extraction of solid sorbents and analysis by the adaptation of SPME methods. SPME was performed with commercially available fibers and easily carried out on a GC/MS instrument. Carboxen™ 569 sorbent is readily available and easy to prepare for sample preservation. The use of solid-phase preservatives eliminates the need to transport organic solvents or acids to the field. The results in this study indicate that samples preserved with Carboxen™ 569 can be stored for hundreds of hours, frozen or at room temperature, with no evident trend in percent VOC recovery.

This study was limited to laboratory-spiked soil samples and a commercially available certified soil standard. “Real world” environmental samples were not available for analysis during the method development. Non-quantitative (variable) VOC recoveries were observed with soils and solid-phase preservatives. The VOC recoveries for experiments with the RTC certified VOA soil were comparable to values reported on the certificate for the Prediction Interval. Analyte loss or non-recovery may be indicative of VOC entrapment in soil micropores. A combination of hot solvent extraction and solid-phase VOC sequestration may be a means of quantifying firm binding. The use of deuterated internal standards and surrogates may help to compensate for sample-to-sample variations in extraction and desorption efficiency.

The formation of a residual firmly-bound fraction is important for soil studies. After the soil was exposed for hundreds of hours to high VOC concentrations, slow desorption of VOCs was observed. These results indicate the firmly-bound or non-labile VOC fractions may not be accounted for in the soil samples analyzed and data reported, which have implications for fate and transport processes and pump-and- treat technology for contaminant remediation.

APPENDIX I

CERTIFICATES OF ANALYSES

Certificate of Analysis

Purgeable Aromatics Mixture

Catalog Number: AMM-602N

Lot Number: P1333

Page: 1

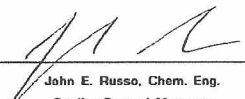
This ULTRAstandard(TM) solution was gravimetrically prepared, and the analyte concentrations were verified using high resolution gas chromatography and/or high performance liquid chromatography. The solution was prepared at the nominal concentration stated on the box label. The true value for each analyte, determined gravimetrically, is listed below.

Component	Weight/mL*
benzene	100.4 µg
chlorobenzene	100.4 µg
1,2-dichlorobenzene	100.4 µg
1,3-dichlorobenzene	100.4 µg
1,4-dichlorobenzene	100.4 µg
ethylbenzene	100.4 µg
toluene	100.4 µg

Solvent: methanol

* Balances used in the manufacture of this standard are calibrated with weights traceable to NIST in compliance with ANSI/NCSL Z-540-1 and ISO 9001.




John E. Russo, Chem. Eng.
Quality Control Manager

Certificate of Analysis

Purgeable Halocarbon Mixture

Catalog Number: HCM-601

Lot Number: P1269

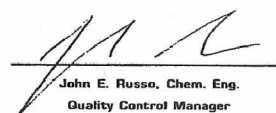
Page: 1

This ULTRAstandard(TM) solution was gravimetrically prepared, and the analyte concentrations were verified using high resolution gas chromatography and/or high performance liquid chromatography. The solution was prepared at the nominal concentration stated on the box label. The true value for each analyte, determined gravimetrically, is listed below.

Component	Weight/mL*
bromodichloromethane	100.3 µg
bromoform	100.3 µg
bromomethane	100.4 µg
carbon tetrachloride	100.3 µg
chlorobenzene	100.3 µg
chloroethane	100.4 µg
chloroform	100.3 µg
chloromethane	100.4 µg
dibromochloromethane	100.3 µg
1,2-dichlorobenzene	100.2 µg
1,3-dichlorobenzene	100.3 µg
1,4-dichlorobenzene	100.4 µg
dichlorodifluoromethane	100.4 µg
1,1-dichloroethane	100.3 µg
1,2-dichloroethane	100.3 µg
1,1-dichloroethene	100.3 µg
trans-1,2-dichloroethene	100.3 µg
1,2-dichloropropane	100.3 µg
cis-1,3-dichloropropene	100.3 µg
trans-1,3-dichloropropene	100.3 µg
methylene chloride	100.3 µg
1,1,2,2-tetrachloroethane	100.3 µg
tetrachloroethene	100.3 µg
1,1,1-trichloroethane	100.3 µg
1,1,2-trichloroethane	100.3 µg

* Balances used in the manufacture of this standard are calibrated with weights traceable to NIST in compliance with ANSI/NCCL Z-540-1 and ISO 9001.




John E. Russo, Chem. Eng.
Quality Control Manager

Certificate of Analysis

Purgeable Halocarbon Mixture

Catalog Number: HCM-601

Lot Number: P1269

Page: 2

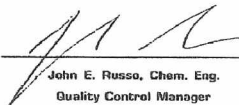
trichloroethene
trichlorofluoromethane
vinyl chloride

100.3 µg
100.5 µg
100.4 µg

Solvent: methanol

* Balances used in the manufacture of this standard are calibrated with weights traceable to NIST in compliance with ANSI/NCSL Z-540-1 and ISO 9001.




John E. Russo, Chem. Eng.
Quality Control Manager

Certificate of Analysis

NATURAL MATRIX CERTIFIED REFERENCE MATERIAL

Catalog No: CRM607-⁹⁰⁵~~900~~
Lot No: AC607

VOA CONTAMINATED SOIL

ANALYTE CONCENTRATIONS

Analyte	Reference		Confidence	Prediction
	Value	S.D.	Interval	Interval
1,1,1-Trichloroethane	97.1	18.9	87.8 - 106	56.3 - 138
1,1,2,2-Tetrachloroethane	202	57.0	175 - 229	80.0 - 325
1,2-Dichlorobenzene	146	30.1	131 - 160	80.4 - 211
1,2-dichloroethane	186	39.1	168 - 205	102 - 270
1,4-Dichlorobenzene	169	33.1	153 - 184	97.0 - 240
4-Methyl-2-pentanone (MIBK)	252	47.5	228 - 275	148 - 355
Benzene	107	22.3	97.1 - 116	58.9 - 154
Bromoform	117	29.6	103 - 131	53.4 - 181
Carbon tetrachloride	237	51.0	213 - 262	128 - 347
Chlorobenzene	158	23.6	147 - 169	107 - 209
Chloroform	111	18.4	102 - 120	71.0 - 151
Ethylbenzene	127	22.4	118 - 137	79.2 - 175
Methylene Chloride	193	63.7	157 - 229	49.6 - 336
Toluene	202	27.4	188 - 215	143 - 261
Trichloroethene	117	15.0	110 - 124	84.7 - 150
Xylenes, total	191	31.6	174 - 208	123 - 259

All values are expressed in $\mu\text{g/kg}$ (parts per billion) on a wet weight basis. The Reference Values were determined by USEPA SW846 (3rd edition) Method 8260B using the low soil concentration procedure. The sample is suitable for these and other similar methods. See Product Information Sheet for explanation of Confidence Interval and Prediction Interval.

"THIS PRODUCT WAS DESIGNED, PRODUCED, AND VERIFIED FOR ACCURACY AND STABILITY IN ACCORDANCE WITH USEPA/AALA RM-03 AND ISO GUIDES 34 AND 35."



Certifying Officer

Use within 3 months of delivery



RESOURCE
TECHNOLOGY
CORPORATION

Store at +4 ° C

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Laramie, WY 82070 USA
(307) 742-5452
FAX (307) 745-7936

MSDS Available Upon Request

APPENDIX II

DATA FOR VOC SLOW DESORPTION EXPERIMENTS

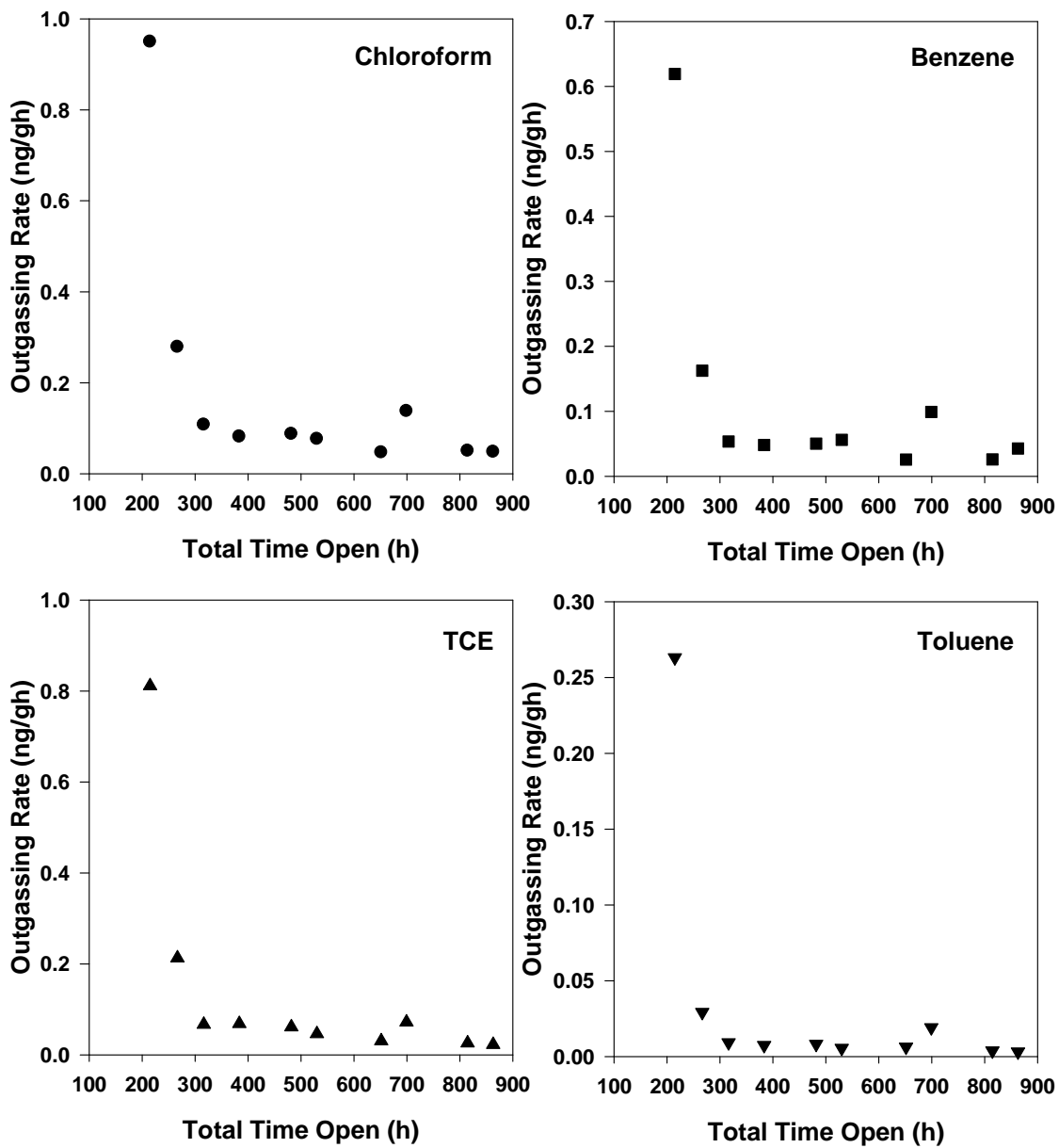


Figure AII-1. Formation of a residual slow-release VOC fraction in Las Vegas soil samples (5 g, 5% water content, and ambient temperature) after prolonged vapor-phase exposure (~1190 hours).

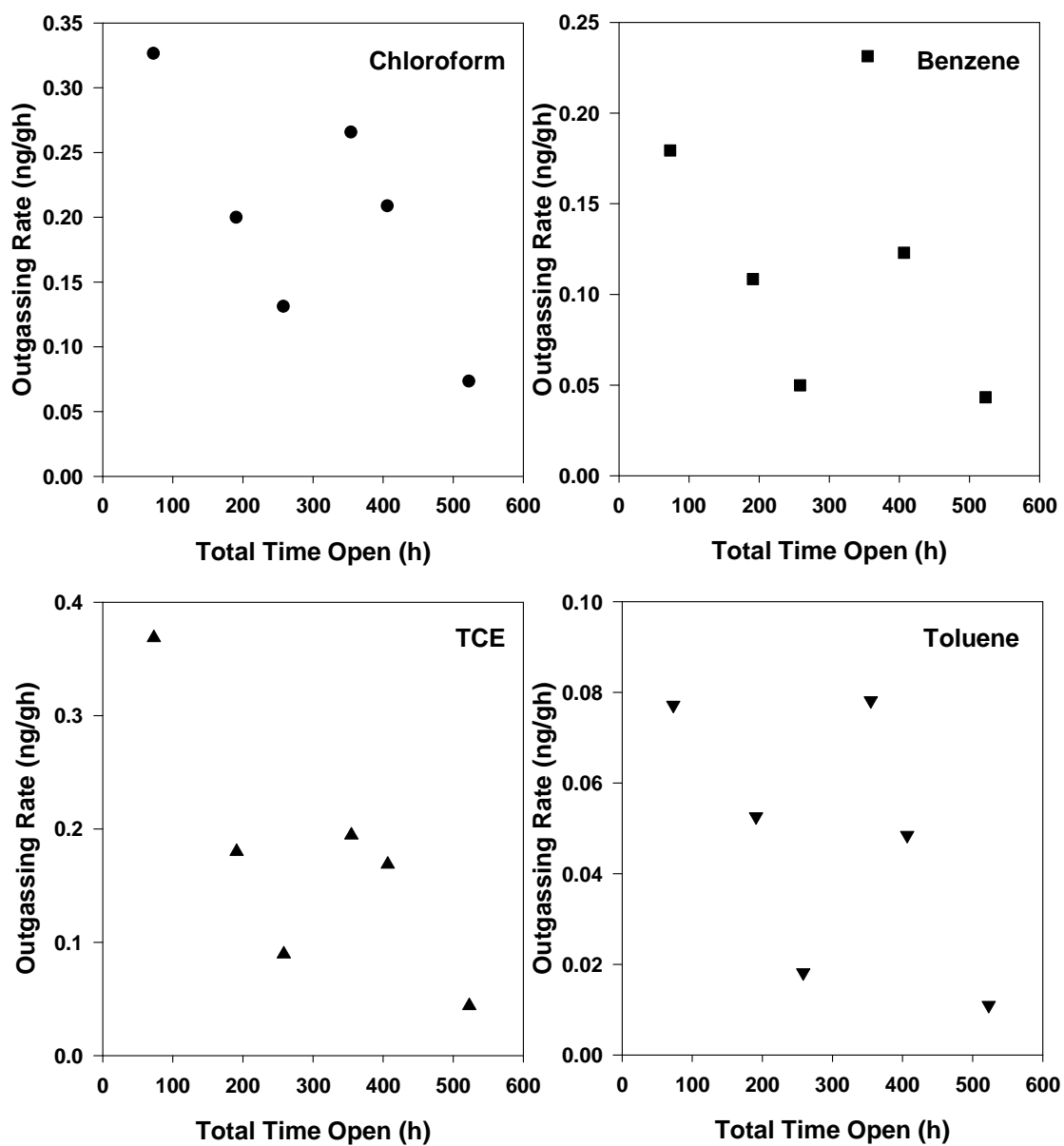


Figure AII-2. Formation of a residual slow-release VOC fraction in Las Vegas soil samples (5 g, 5% water content, and ambient temperature) after prolonged vapor-phase exposure (~1190 hours).

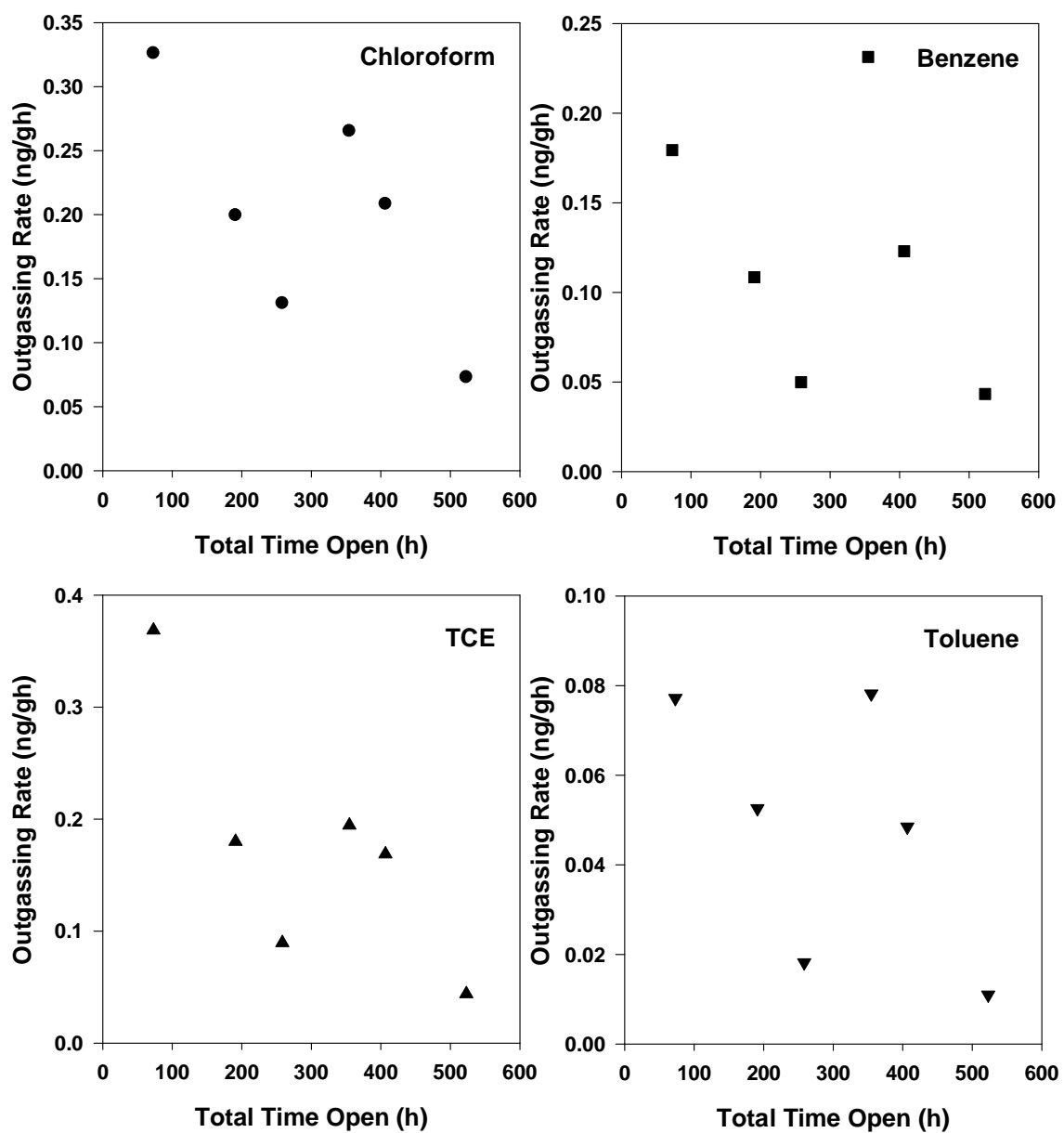


Figure AII-3. Formation of a residual slow-release VOC fraction in Las Vegas soil samples (5 g, 5% water content, and ambient temperature) after prolonged vapor-phase exposure (~1190 hours).

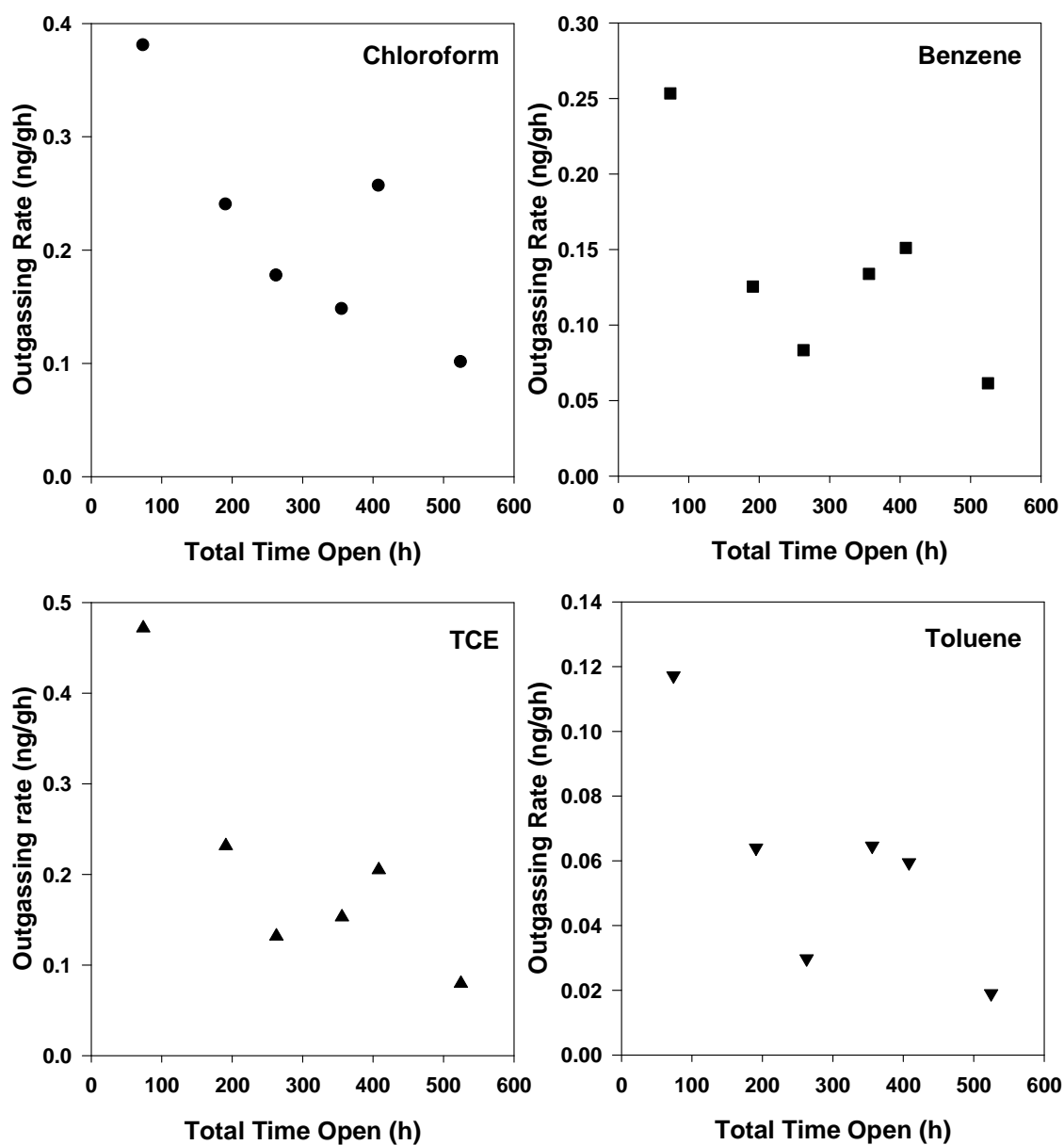


Figure AII-4. Formation of a residual slow-release VOC fraction in Las Vegas soil samples (5 g, 5% water content, and ambient temperature) after prolonged vapor-phase exposure (~1190 hours).

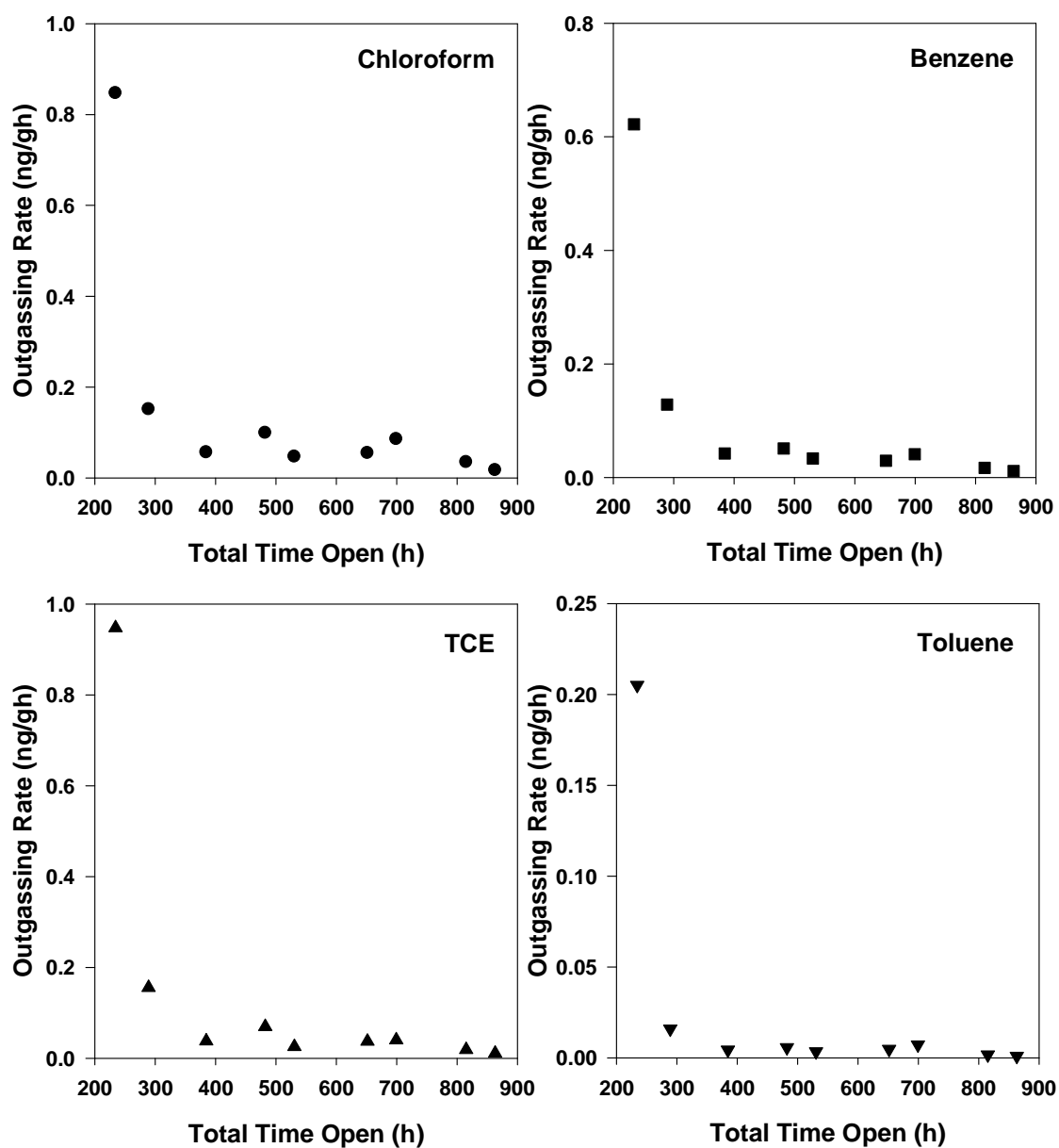


Figure AII-5. Formation of a residual slow-release VOC fraction in Las Vegas soil samples (5 g, 10% water content, and ambient temperature) after prolonged vapor-phase exposure (~1190 hours).

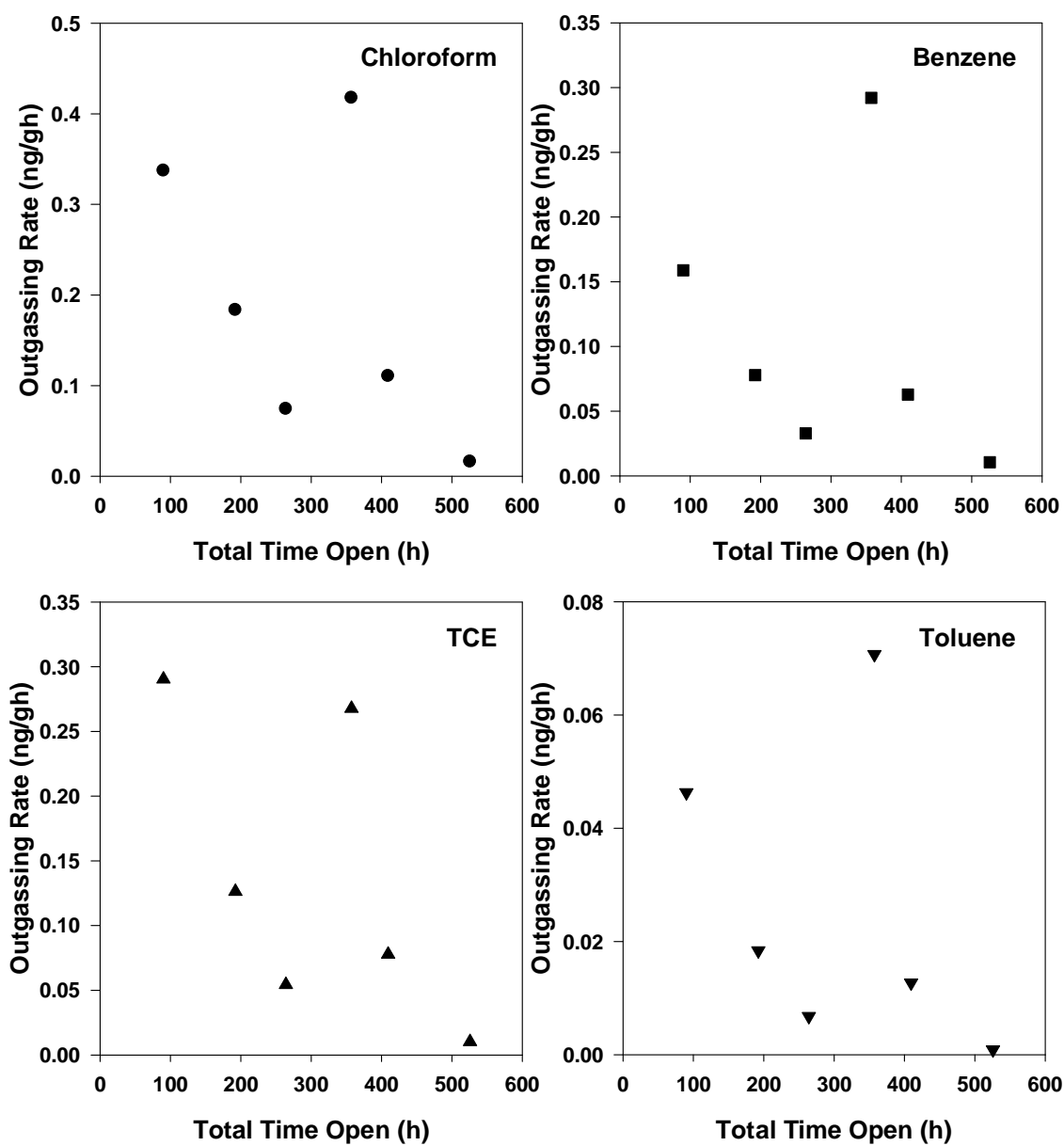


Figure AII-6. Formation of a residual slow-release VOC fraction in Las Vegas soil samples (5 g, 10% water content, and ambient temperature) after prolonged vapor-phase exposure (~1190 hours).

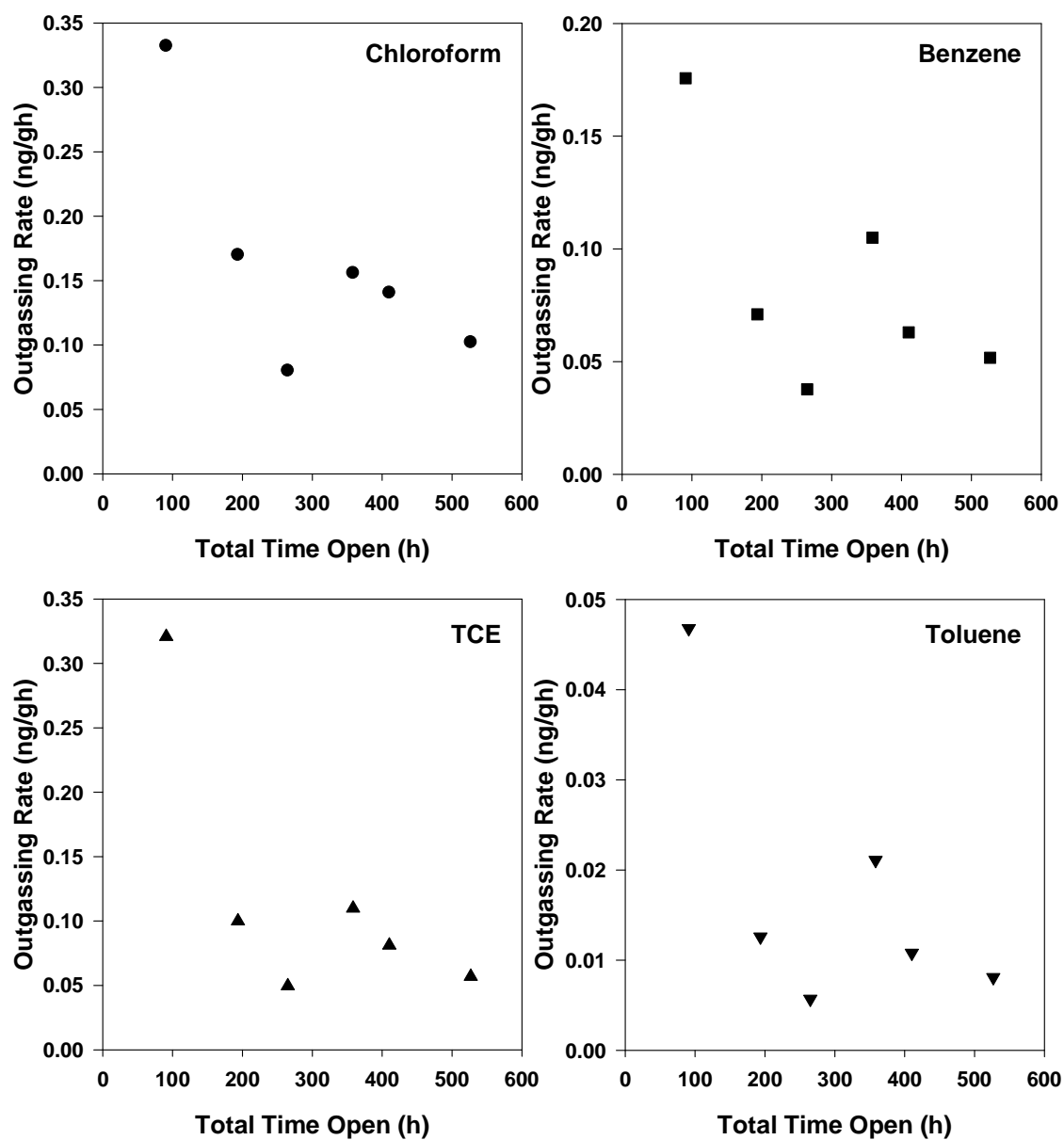


Figure AII-7. Formation of a residual slow-release VOC fraction in Las Vegas soil samples (5 g, 10% water content, and ambient temperature) after prolonged vapor-phase exposure (~1190 hours).

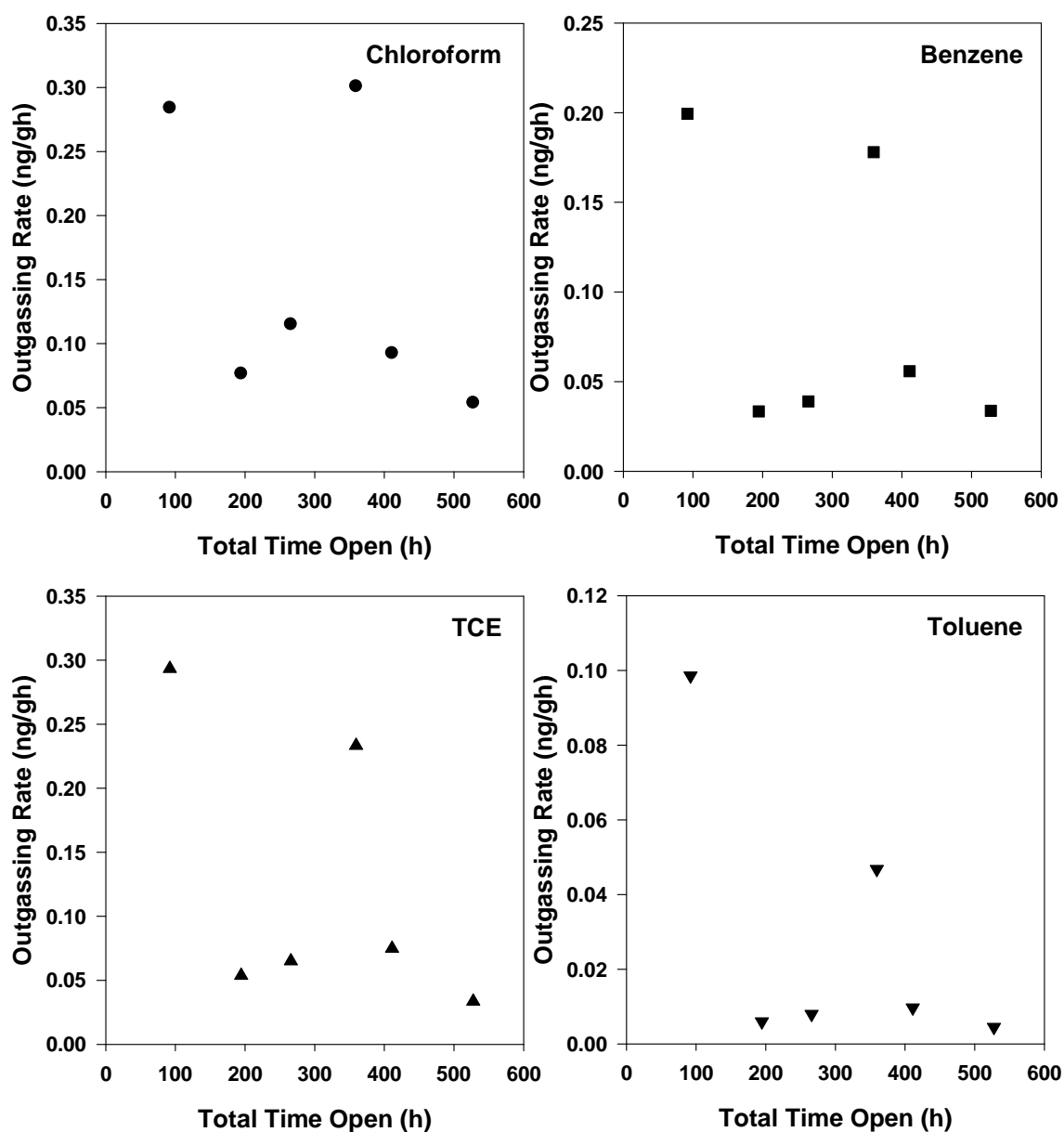


Figure AII-8. Formation of a residual slow-release VOC fraction in Las Vegas soil samples (5 g, 10% water content, and ambient temperature) after prolonged vapor-phase exposure (~1190 hours).

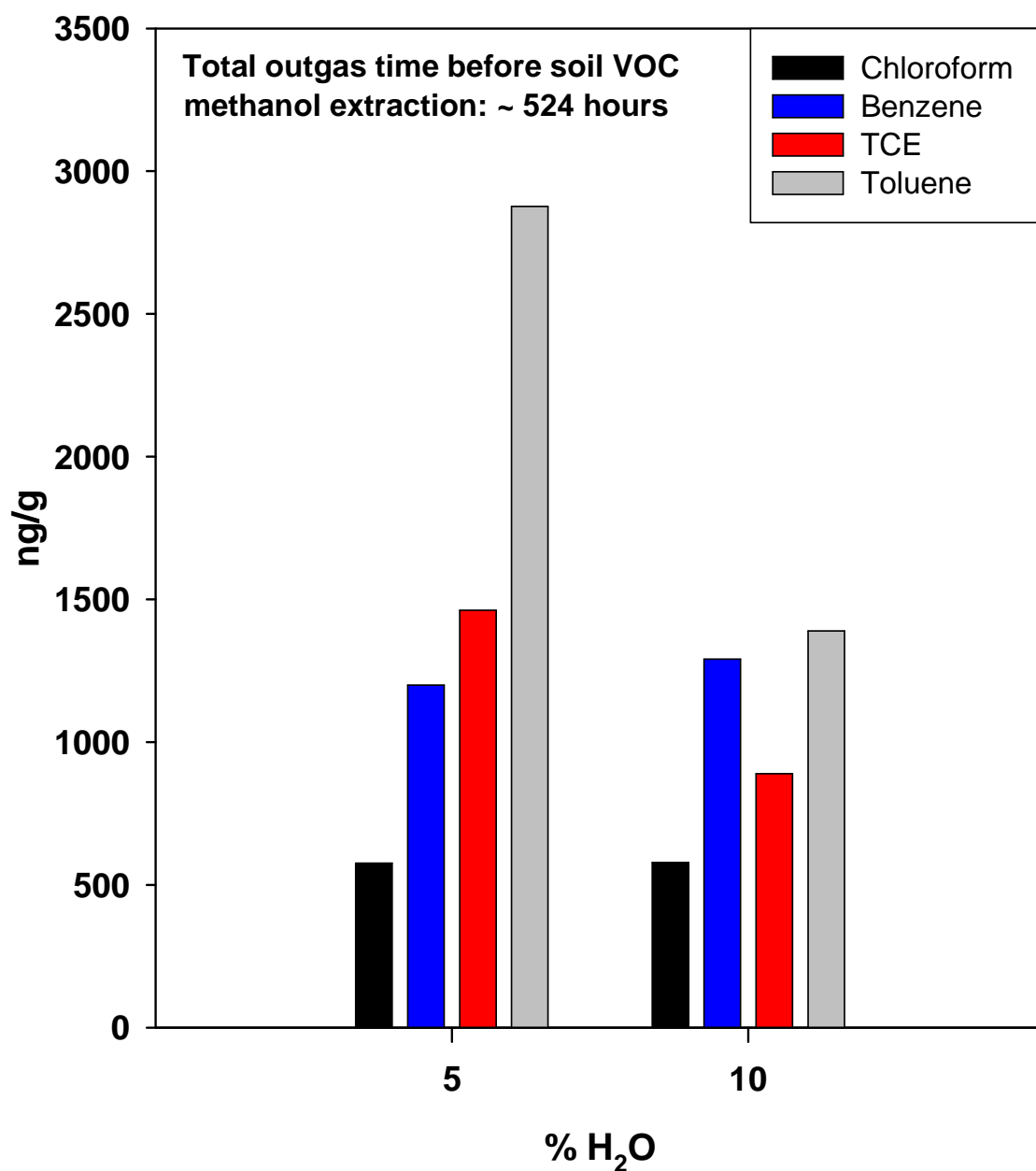


Figure AII-9. Recoveries of residual VOCs in methanol extractions of Las Vegas soil samples (5 g, 5% and 10% water content, and ambient temperature) after prolonged vapor-phase exposure (~1190 hours). Total outgas time for the soil samples before VOC methanol extraction was ~524 hours.

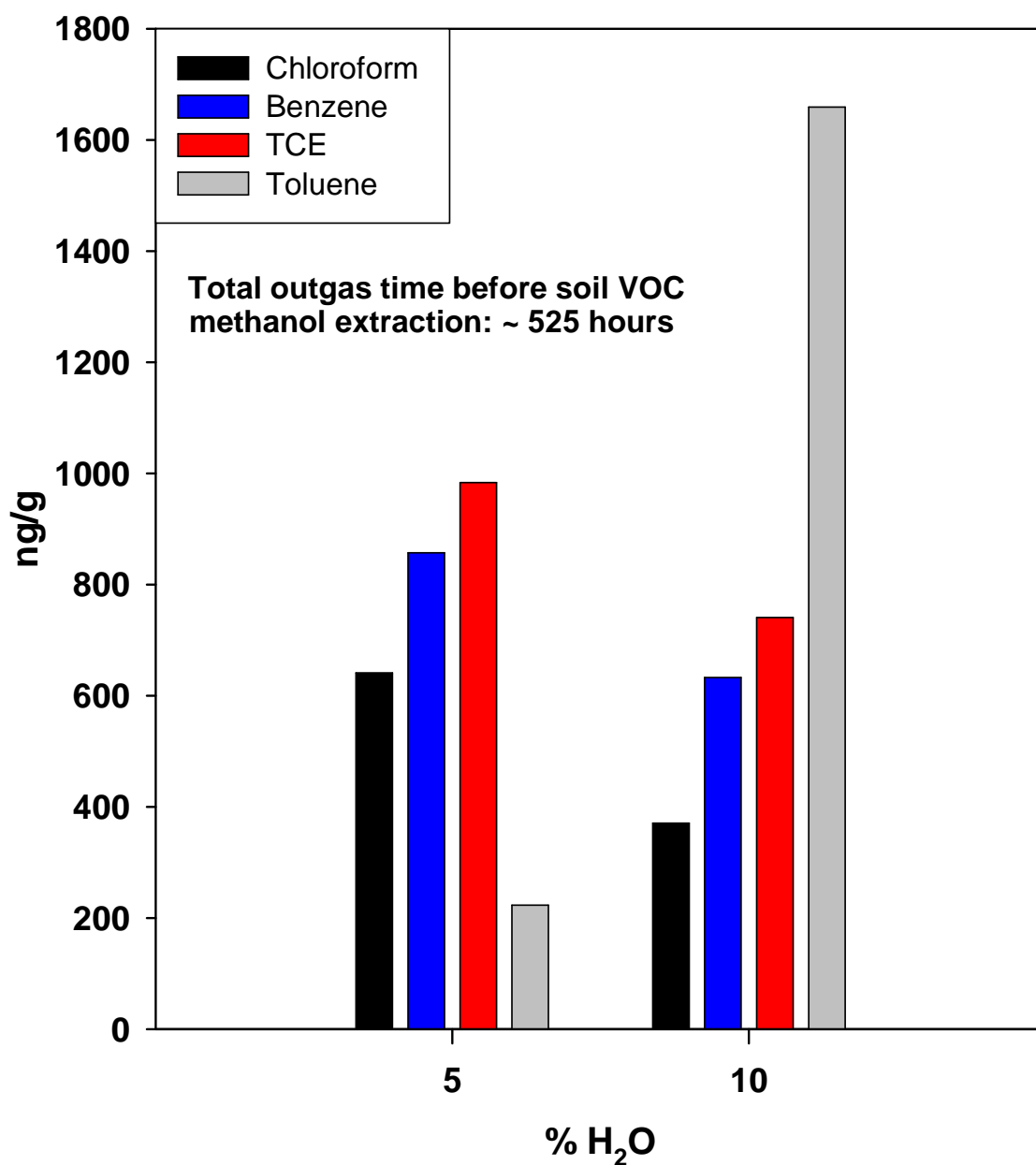


Figure AII-10. Recoveries of residual VOCs in methanol extractions of Las Vegas soil samples (5 g, 5% and 10% water content, and ambient temperature) after prolonged vapor-phase exposure (~1190 hours). Total outgas time for the soil samples before VOC methanol extraction was ~525 hours.

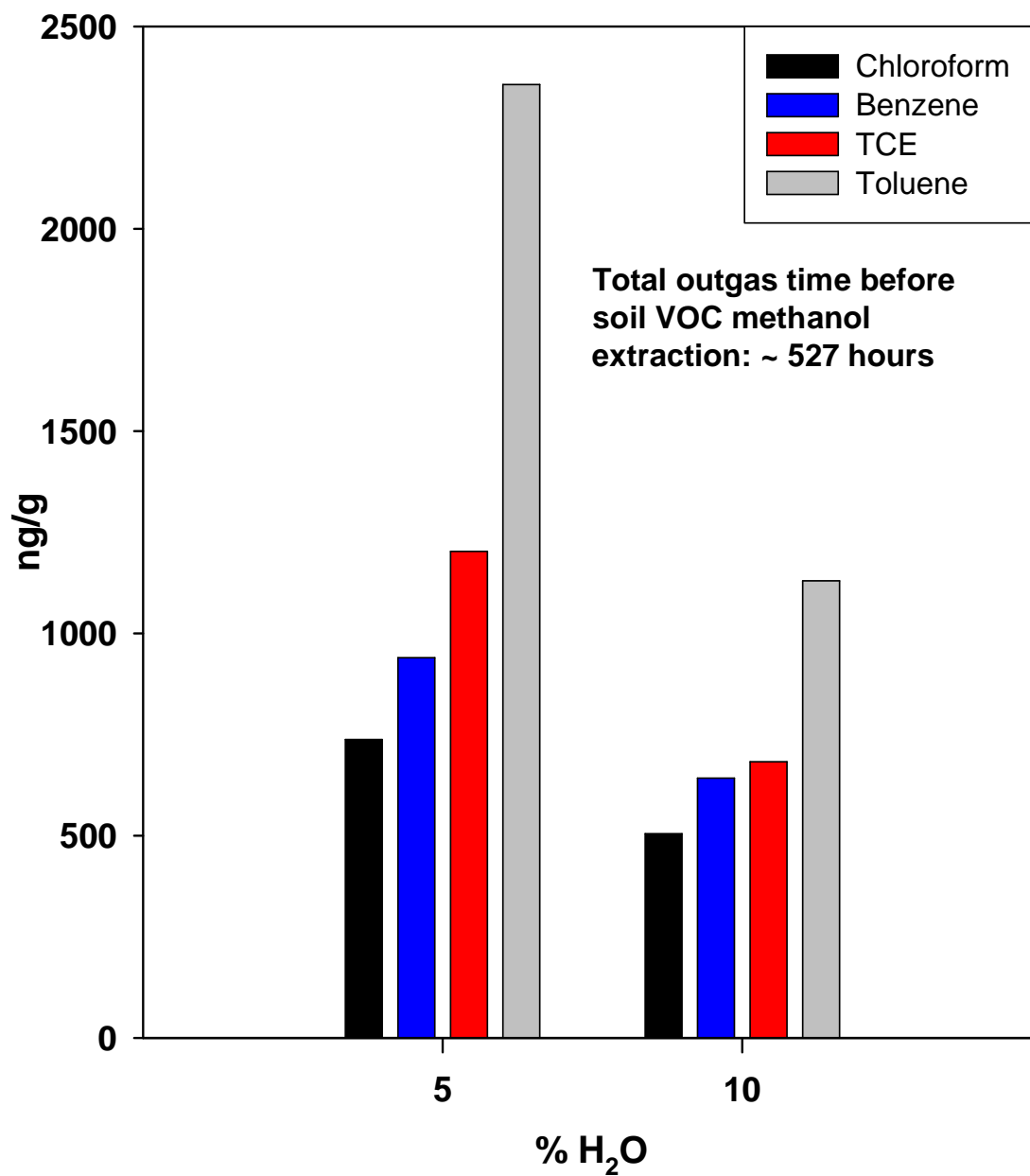


Figure AII-11. Recoveries of residual VOCs in methanol extractions of Las Vegas soil samples (5 g, 5% and 10% water content, and ambient temperature) after prolonged vapor-phase exposure (~1190 hours). Total outgas time for the soil samples before VOC methanol extraction was ~527 hours.

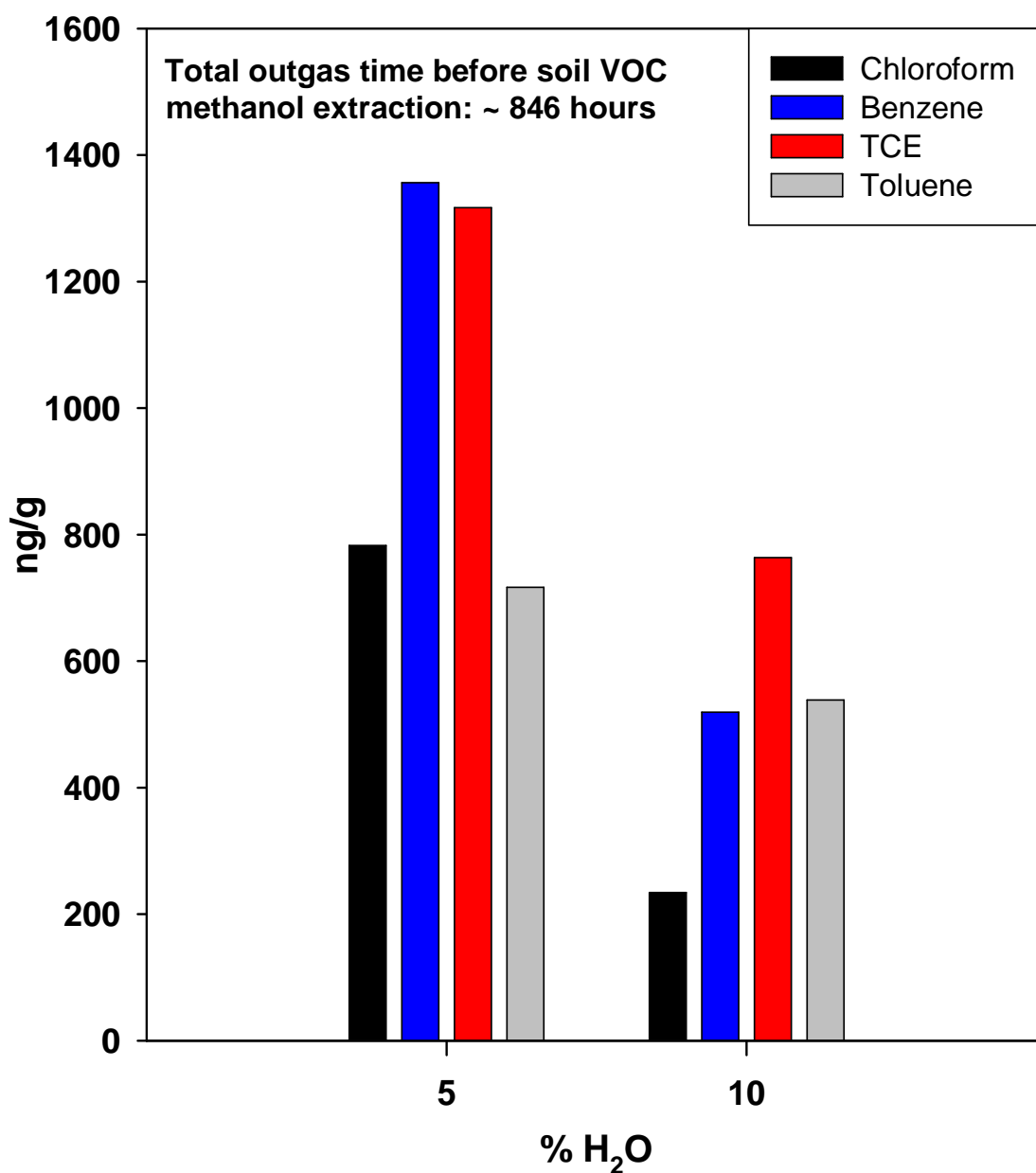


Figure AII-12. Recoveries of residual VOCs in methanol extractions of Las Vegas soil samples (5 g, 5% and 10% water content, and ambient temperature) after prolonged vapor-phase exposure (~1190 hours). Total outgas time for the soil samples before VOC methanol extraction was ~846 hours.

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Steinberg, S. M.; Schmett, G. T.; Kimble, G. M.; Emerson, D. W.; Turner, M. F.; Rudin, M., Immobilization of fission iodine by reaction with insoluble natural organic matter. *J. Radioanal. Nucl. Chem.* **2008**, 277(1), 175-183.

Turner, M.; Rudin, M.; Cizdziel, J.; Hodge, V., Excess plutonium in soil near the Nevada Test Site, USA. *Environ. Pollut.* **2003**, 125 (2), 193-203.

Thesis Title: Analytical Method Development for Determination of Volatile Organic Compounds in Calcareous Desert Soil

Thesis Examination Committee:

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Committee Member, Dr. Vernon F. Hodge, Ph.D.
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