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Accelerated Solvent Extraction: A Technique for Sample Preparation

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We describe a new technique for sample preparation, accelerated solvent extraction (ASE), that combines elevated temperatures and pressures with liquid solvents. The effects of various operational parameters (i.e., temperature, pressure, and volume of solvent used) on the performance of ASE were investigated. The solvents used are those normally used for standard liquid extraction techniques like Soxhlet or sonication. We found the recoveries of polycyclic aromatic hydrocarbons, polychlorinated biphenyls, and total petroleum hydrocarbons from reference materials using ASE to be quantitative. The extraction time for 1−30-g samples is less than 15 min, and the volume of solvent is 1.2−1.5 times that of the extraction cell containing the sample. No evidence was seen for thermal degradation during the extraction of temperature-sensitive compounds.

Sample extraction procedures are often perceived as bottlenecks in analytical methods. In the last few years, various attempts have been made to replace classical extraction techniques (for example, automated Soxhlet extraction,[1,2] microwave dissolution,[3−6] sonication extraction,[7−9] and supercritical fluid extraction.[10−12]). Each technique reduces the volume of extraction solvent required and shortens the sample preparation time as compared to Soxhlet extraction. There is an interesting commonality regarding temperature for three of these procedures, namely automated Soxhlet, supercritical fluid extraction (SFE), and microwave extraction.

Automated Soxhlet extraction can be faster (2−4 h) and use less solvent (50−100 mL) than conventional Soxhlet extractions because the sample is immersed in a boiling solvent during the first portion of the extraction setup. Recent work in SFE has shown improved recovery with increases in temperature.[13−15] Extraction times in microwave extraction are shortened compared to those in Soxhlet extraction because the solvent can be heated above its boiling point with the use of pressurizable vessels. These data indicate that increased temperature during extractions gives favorable gains relative to time and solvent usage.

In this paper, we report on the development of accelerated solvent extraction (ASE), a new extraction procedure that uses organic solvents at high pressures and temperatures above the boiling point. ASE has been shown to be equivalent to standard EPA extraction methodology in terms of recovery and precision, and it has appeared as proposed Method 3545 in Update III of the U.S. EPA SW-846 Methods.[16,17] However, no reports of the work performed to develop ASE have been published to date.

With ASE, a solid sample is enclosed in a sample cartridge that is filled with an extraction fluid and used to statically extract the sample under elevated temperature (50−200 °C) and pressure (500−3000 psi) conditions for short time periods (5−10 min). Compressed gas is used to purge the sample extract from the cell into a collection vessel. Currently, ASE is applicable to solid or semisolid samples that can be retained in the cell during extraction.

This paper gives the first details of accelerated solvent extraction as a technique and the effect of experimental parameters on recovery. Temperature, pressure, solvent volume, prefill, and preheat methodologies were investigated to assess the effect of experimental conditions on the performance of ASE. In addition, we studied thermal degradation during extraction. The recoveries of total petroleum hydrocarbons (TPHs), polycyclic aromatic hydrocarbons (PAHs), and polychlorinated biphenyls (PCBs) from certified samples are also reported.

PHYSICOCHEMICAL CONSIDERATIONS FOR ENHANCED EXTRACTIONS AT ELEVATED TEMPERATURES AND PRESSURES

There are two main reasons why the use of liquid solvents at elevated temperatures and pressures should give enhanced

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performance compared to extractions at or near room temperature and atmospheric pressure: (1) solubility and mass transfer effects and (2) disruption of surface equilibria.

Solubility and Mass Transfer Effects. (A) The use of higher temperatures increases the capacity of solvents to solubilize analytes. For example, based on calculations of the temperature dependency of solubility[18] of an ideal solution, the solubility of anthracene increases almost 13-fold as the temperature increases from 50 to 150 °C. The solubility of hydrocarbons such as *n*-eicosane can increase several hundred-fold in the same temperature range.[18]

In addition, Sekine and Hasegawa[19] pointed out that the solubility of water in organic solvents will increase with increasing temperature. This would be pertinent in the cases in which solvents at low temperatures and pressures are excluded from water-sealed pores that contain analytes. The increased solubility of water in organic solvents caused by elevated temperatures would facilitate the availability of these sealed pores and the analytes contained therein.

(B) Faster diffusion rates occur as a result of increasing the temperature of the extraction. It can be difficult to obtain an exact relationship for the effect of temperature on diffusion rates, especially with finite concentrations and a multicomponent system. However, by way of illustration, diffusion rates have been shown to increase roughly 2−10-fold upon increasing the temperature from 25 to 150 °C.[20]

(C) If fresh solvent were introduced during a static extraction step (this is analogous to what occurs in Soxhlet extraction), improved mass transfer and, hence, increased extraction rates would result. The introduction of fresh solvent will increase the concentration gradient between the solution present in the cell (which would be effectively diluted when some of the solution escapes and fresh solvent enters the cell inlet) and the surface of the sample matrix. The larger the concentration gradient, the faster the mass transfer rate or flux according to Fick's first law of diffusion.[21]

Disruption of Surface Equilibria. Since both temperature and pressure play a significant role, we will discuss these parameters separately.

Temperature Effects. (A) Increased temperatures can disrupt the strong solute−matrix interactions caused by van der Waals forces, hydrogen bonding, and dipole attractions of the solute molecules and active sites on the matrix. Thermal energy can overcome cohesive (solute−solute) and adhesive (solute−matrix) interactions by decreasing the activation energy required for the desorption process. In addition, hydrogen bonding is weakened with increased temperature, as noted by Pimentel and McClellan.[22]

(B) Higher temperatures also decrease the viscosity of liquid solvents, thus allowing better penetration of matrix particles and enhancing extraction. As a point of reference, the viscosity of 2-propanol decreases by a factor of 9 as the temperature increases from 25 to 200 °C.[20] In addition to reducing viscosity, increased temperatures will also decrease the surface tension of the solvent, solutes, and matrix, allowing the solvent to better "wet" the sample matrix. Both changes will facilitate better contact of the analytes with the solvent and enhance extraction. A decrease in solvent surface tension will also allow solvent cavities to form more easily,[23] thus permitting analytes to be more quickly dissolved in the solvent.

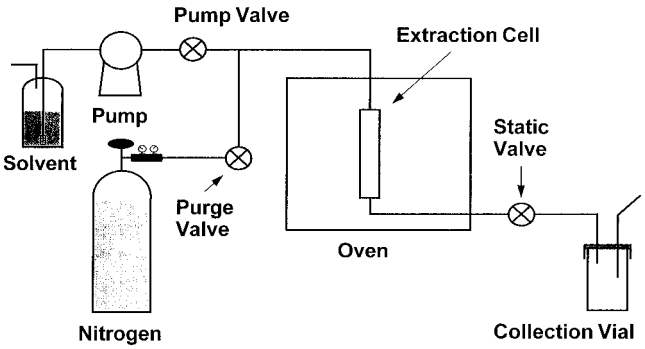

Figure 1. Schematic of accelerated solvent extraction (ASE) system.

Pressure Effects. (A) If sufficient pressure is exerted on the solvent during extractions, temperatures above the boiling point can be used. The use of elevated temperatures and the associated advantages would be precluded without the use of elevated pressures to maintain the solvents as liquids.

(B) The use of pressure should facilitate extractions from samples in which the analytes have been trapped in matrix pores. The pressure forces the solvent into areas of the matrices that would not normally be contacted by solvents using atmospheric conditions. For example, if analytes are trapped in pores, and water (or even an air bubble for small pores) has then "sealed" the pore entrance, solvents may not be able to contact these analytes and extract them. The use of elevated pressures (along with elevated temperatures and the reduced solvent surface tensions) will help force the solvent into the pore to contact the analytes.

(C) For samples in which the analytes are found on the surface or in pores that are readily accessible, the pressure gives an advantage, as is seen in liquid chromatography. A good analogy would be the comparison of standard column liquid chromatography to flash chromatography or even high-performance liquid chromatography (HPLC). In the case in which analytes are found mostly on the surface, the process of pressurized liquid extraction can best be described as adsorption chromatography. Pressurized flow aids in the solubilization of air bubbles so that solvent more rapidly comes in close contact with the entire sample matrix.

EXPERIMENTAL SECTION

Materials and Methods. Figure 1 is a schematic of ASE. All tubing was $^1/_{16}$-in.-o.d. stainless steel of 0.02 in. i.d. No back-pressure regulators or restrictors were used in the design. The pneumatic valves (Valco, Houston, TX) used were automatically actuated with timing circuits built into the control electronics (built in-house). The static valve was a high-pressure on/off valve (Part No. ASFVO), and the pump and purge valves were high-pressure prime/purge valves (Part No. ASFV). For the experiments reported here, the extraction cells were stainless steel rated at 5000 or 10 000 psi, with volumes of 3.5 (9.4 mm i.d. × 50 mm),

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7.0 (9.4 mm i.d. × 100 mm), 10.4 (9.4 mm i.d. × 150 mm), 16.0 (14 mm i.d. × 100 mm), and 32 (14 mm i.d. × 200 mm) mL (Keystone Scientific, Inc., Bellefonte, PA). Tubing connections to the cells were made with fingertight fittings (Slipfree connectors, Keystone Scientific). The extraction cells were heated in either a gas chromatographic oven (HP 5890, Hewlett-Packard, Wilmington, DE) or a heating block (built in-house). The pumps used were HPLC pumps operated under pressure control rather than flow control (designed and built in-house). All samples were collected in septum-topped 30- or 40-mL vials (Baxter Diagnostics, Scientific Products, McGaw, IL, or I-Chem, Hayward, CA).

Safety Considerations. A hydrocarbon gas sensor was used to monitor for solvent leaks. The device was designed in-house and was based on a Figaro TGS822 semiconductor sensor (Figaro USA, Inc., Wilmette, IL). Since organic solvents at elevated temperatures and pressures were used, appropriate safety shields were in place to protect the users from any spraying of solvents. Care was taken to prevent overpressurization of cells during the heating of organic solvents. Electronic and physical pressure relief safeguards were in place. Anyone attempting to perform such experiments should observe the same safety precautions.

Samples were loaded into the extraction cells, and any extra volume was filled with clean sand at the inlet end of the cell (Fisher Scientific, Fair Lawn, NJ). When the cells were loaded and tightened, extractions were performed by either preheating the cell before filling with solvent (preheat method) or by filling the cell with solvent before heating (prefill method).

In the preheat procedure, the sample cell was immediately loaded into the oven and heated to the extraction temperature (the range of 30−200 °C was tested). When a gas chromatographic oven was used, the cell was allowed to equilibrate for 15 min after the oven reached the set point temperature. When a heated block was used, the block heater remained at the set point temperature, and the cell was placed in the block assembly. The cell was allowed to equilibrate for 5 min before proceeding. (Temperature measurements of sand-filled cells showed that the cell internal temperature was at the set point within 3 min in the heated block and within 12 min in the GC oven.) The static valve was opened during the preheat step. The pump valve was opened after the heat-up time, and solvent was introduced into the cell at ∼8 mL/min until about 1 mL had accumulated in the collection vial, at which point the static valve closed and the cell continued to pressurize to the set point (200−3000 psi). The static period for these studies was 5 min, because longer periods did not show improvements in recoveries. After the static period, the static valve was reopened, fresh solvent was introduced to flush the lines and cell, and the extract was collected in the vial. During this solvent flush step, 50−100% of the extraction cell volume of solvent was pumped into the cell. The pump valve was then closed, the purge valve was opened, and pressurized nitrogen (125−150 psi) forced the solvent out of the extraction cell and into the collection vial.

The prefill method was similar to the above procedure. However, the cell was filled with solvent before being loaded into the oven, and ∼1 mL was collected as with the preheat method. A heating block was used for all prefill experiments, so a 5-min heat-up time was used. During the heat-up period, the solvent in the cell expanded, and the cell pressure increased. To prevent overpressurization of the cell, the static valve pulsed open and closed automatically when the cell pressure exceeded the set point by 200 psi. The solvent that escaped during this venting (0.1−0.2 mL/cycle of valve) was collected in the vial. Since the pump valve remained opened, fresh solvent was pumped into the cell to maintain pressure. Venting of the solvent continued until the cell had equilibrated to the oven temperature (usually 3 min). A 5-min static period followed the heat-up time. After the static step, the same solvent flush and gas purge steps were followed as with the preheat method.

Initially, we thought that cooling would be necessary for the collection vial due to hot solvent coming from the extraction cell. The temperature of the organic solvent escaping from the cell was measured and found to be less than 35 °C, even with the extraction cell at 100 °C. The fast loss of heat was due to the length of tubing from the cell to the collection vial, ∼30 cm, and the low heat capacity of organic solvents. No difference was seen with or without cooling on the collection vials in terms of recovery or precision when extracting volatile compounds. Therefore, no cooling was used on the collection vials for either preheat or prefill procedures.

Another configuration was considered but not tested. In this setup, the solvent could be heated in a chamber in the oven and then pumped into the extraction cell. With the volumetric flow rates used, it was considered too difficult to maintain a constant temperature in the cell with this configuration.

The effect of a thermal equilibration chamber prior to the extraction cell was investigated. Different lengths of $^1/_{16}$-in.-o.d. tubing (0.5−4 m) were placed in the oven prior to the cell to ensure that the solvent was at the operating temperature before entering the cell. No differences in recovery or precision were seen in the cases with the equilibration chamber as compared to those without. Therefore, no equilibration chamber was used for subsequent experiments.

All solvents were analytical grade or better. Soils with certified values of TPH were purchased from Environmental Research Associates (ERA, Arvada, CO) and stored at 4 °C until used. The hydrocarbons in this sample were in the range of vacuum oil, between C_{20} and C_{50}. U.S. EPA-certified PAH-contaminated soil (SRS100-103, Lot No. Aq103 and RQ103), manufactured by Resource Technology Corp. (Laramie, WY), was purchased from Fisher Scientific (Fair Lawn, NJ). The oyster tissue sample was obtained from the National Oceanic and Atmospheric Administration (NOAA, in Seattle, WA). It was a homogenized tissue sample containing known levels of PCBs. It arrived as a frozen sample and was stored at −5 °C until analyzed. The sample was allowed to thaw, mixed 1:1 with diatomaceous earth, and loaded into an extraction cell. Standard reference material (SRM) 1649, urban dust, was purchased from the National Institute of Standards and Technology (NIST, Gaithersburg, MD) and was used without any pretreatment.

The Canadian marine sediment sample (HS-3) was obtained from the National Research Council Canada (NRCC, Halifax, NS, Canada). It was a dried, ground, and homogenized marine sediment sample containing certified levels of PAHs. The sample was stored at 4 °C until used, and no pretreatment was done on the sample prior to extraction. The sewage sludge sample was obtained from the Fresenius Institute (Taunusstein, Germany) and used as it came. It had been air-dried at 40 °C overnight and ground and sieved to 50 mesh. This sample received no pretreatment prior to extraction.

A pulverized rock sample containing bitumen (Chattanooga shale) was extracted to further investigate the effect of temperature on analyte recovery. This sample contains aromatic and aliphatic hydrocarbons which elute below C_{32} under GC conditions. The level of hydrocarbon, as determined by automated Soxhlet extraction with toluene, was 4058 ppm (mg/kg).

In the experiments performed to investigate the effect of pressure relative to the pore size of the matrix and the molecular size of the analytes, silica (Keystone Scientific) with a particle range of 15−25 μm and different pore sizes (100, 300, and 1000 Å) was loaded with PAHs. A dilute solution containing the PAHs (Supelco, Bellefonte, PA) in methylene chloride was poured over each of the silicas. The resulting mixture was stirred well, and the solvent was allowed to evaporate. One-gram portions of the silica were extracted by ASE using methylene chloride/acetone (1:1 v/v) at 100 °C with the prefill method with 5 min of thermal equilibration, 5 min static, and a 60-s nitrogen purge. The extractions were done at 500, 1000, 1500, 2000, and 2500 psi on fresh samples. In addition, fresh portions of the PAH-loaded silica were loaded with water. This was accomplished by completely immersing the PAH-loaded silicas in water, followed by a 5-min sonication treatment to ensure penetration of water into the pores and evaporation of excess water by nitrogen blow-down. All silicas were maintained at ~60% water by weight to ensure uniform results. Extractions were then performed by ASE on these samples using the same set of conditions as listed. These experiments were performed to assess the effect of elevated pressures on recovery of analytes adsorbed to different pore size matrices.

Quantitation. PAH analyses of the silica and urban dust extracts were performed by liquid chromatography using a Dionex DX-300 system (Dionex, Sunnyvale, CA) on a 15-cm × 4.6-mm LC-PAH column (Supelco) at a flow rate of 1.5 mL/min. The mobile phase consisted of 60% water/40% acetonitrile for 5 min, followed by a linear gradient to 100% acetonitrile over 25 min. Detection was by combined UV at 254 nm and fluorescence with 325-nm excitation and 410-nm emission. Quantitation was performed by external standard calibration.

PCB analyses of the oyster tissue and sewage sludge extracts were performed by gas chromatography (GC) with an electron capture detector (ECD) using a Hewlett-Packard 5890 gas chromatograph with a 30-m × 0.25-mm i.d. RT_X-5 capillary column (Restek, Bellefonte, PA). The injector and detector were maintained at 350 °C. The system was ramped from 100 to 300 °C at 10 °C/min following a 5-min hold. Quantitation was performed by external standard calibration.

Extracts of the Chattanooga shale were analyzed by GC (HP 5890) with a flame ionization detector (FID) and by measuring their absorbance at 600 nm. The GC conditions were as follows: 30-m × 0.25-mm i.d. Rt_x-5 capillary column, FID at 375 °C, split injector at 350 °C with 10:1 split, 1-μL injection, temperature programmed from 40 to 350 °C at 8 °C/min after a 4-min hold. Helium was the carrier gas at 30 cm/s. Relative peak areas were determined on the GC by comparing the total peak area (excluding the solvent peak) with an internal standard (tetracosane) and dividing by the sample weights in grams. The absorbance measurements were made after diluting the extracts to a constant volume and then filling an HPLC UV detector cell (10 mm path length) with the extracts.

Quantitation of the TPH content was done using a Foxboro (South Norwalk, CT) Miran I fixed-wavelength IR analyzer. The wavelength was 2940 cm^{-1}, and the cell path length was 10 mm. After the extractions, in which perchloroethylene (PERC) from Fluka (Ronkonkoma, NY) was used as the solvent, the extracts were diluted to 10 mL and passed through a disposable pipet containing sodium sulfate and silica gel. An aliquot of the extract was then placed in the IR analyzer. The TPH value was determined by comparing to a three-point calibration curve constructed from dilutions of a stock solution of a 2:3:3 volume ratio of chlorobenzene, isooctane, and *n*-hexadecane.

A standard containing volatile compounds representing gasoline range organics (GRO) and the low end of diesel range organics (DRO) was spiked (100 μL of a 1 mg mL^{-1} $component^{-1}$ solution) onto clean sand to investigate the recovery of these compounds under ASE conditions. The quantitation was done by GC under the following conditions: 30-m × 0.25-mm i.d. Rt_x-5 (Restek) capillary column (1-μm film), FID and splitless injector at 300 °C, 5-μL injection, temperature programmed from 40° to 200 °C at 8 °C/min after 4-min hold with 1-min hold at final temperature. Helium was the carrier gas at 30 cm/s. Acetophenone was added to the vials after collection as an internal standard. The same conditons were used to determine the recovery of pentane spike on the sand.

The Canadian marine sediment extracts were analyzed by GC/MS which conformed to U.S. EPA SW-846 Method 8270C.[24] An HP 5890 Series II GC equipped with a split−splitless injector, an HP 7673 autosampler, and an HP 5970 mass-selective detector were used for the analyses. Sample injection volume was 1 μL. A 30-m × 0.25-mm i.d. XTI-5 (Restek) capillary column was used without a guard column. The GC injector was at 270 °C, and the transfer line was maintained at 300 °C. The GC oven was programmed using the following three-ramp program: from 50 to 310 °C at 10 °C/min after a 3-min hold, then to 326 °C at 4 °C/min, then to 350 °C at 10 °C/min with a 10-min final hold. Helium was used as the carrier gas with a linear velocity of about 30 cm/s. The multiplier voltage on the mass spectrometer was held at 2000 eV, and the system was scanned from 35 to 500 amu. An HP 1000 computer system running RTE-A software was used for data collection and reporting.

RESULTS AND DISCUSSION

Initially, the following conditions were used for the extractions: 100 °C, 2500 psi with a 5-min static period. The solvents chosen were those normally used with conventional methods, like Soxhlet or sonication. Extractions of the ERA standard TPH soil were conducted to determine the analyte content of the various portions of solvent collected in the ASE extraction process. Three fractions were collected and analyzed separately by IR: the portion that came through the cell (1) after heat-up (1.5−2 mL), (2) with the flush step (2 mL), and (3) with the gas purge (1.5−2 mL). Two different samples were extracted using PERC, and the level of TPH was determined in each fraction. A heavily contaminated soil (SRS100-103) with a level of 4% TPH and a less contaminated soil (ERA soil at 1200 ppm) were used (5 g of the ERA and 1 g of the SRS). The experiments were repeated three times on each sample. The results are summarized in Table 1. As can be seen, a large portion of the analytes is extracted in the first 1.5−2-mL portion of the solvent.

(24) Test Methods for Evaluating Solid Waste, Method 8081 and Method 8270C. *USEPA SW-846*, 3rd ed., Update III; U.S. GPO: Washington, DC, July 1995.

Table 1. Total TPH Level (%) Found in Each Fraction[a]

fraction no. (total vol, mL)	ERA soil (1200 mg/kg)	RSD (%)	SRS soil (40 000 mg/kg)	RSD (%)
1 (1.5−2)	72	1.7	88	1.5
2 (3.5−4)	15	1.8	11	1.6
3 (5−6)	13	2.0	1	2.1

[a] Each experiment was repeated three times. The average recovery compared to the certified value was 101.7% with 1.8% RSD for the ERA soil and 103.7% with 1.6% RSD for the SRS soil.

Table 2. Effect of Pressure on PAH Recovery from Water-Covered Silica (300 Å)[a]

	pressure (psi)			
compound	1000	1500	2000	2500
fluorene	0.89	0.92	0.87	0.98
phenanthrene	0.92	0.97	0.91	0.96
anthracene	0.87	0.89	0.85	0.87
fluoranthene	1.05	1.08	1.21	1.23
benz[*a*]anthracene	1.00	1.07	1.38	1.59
chrysene	0.98	1.02	1.64	1.46
benzo[*b*]fluoranthene	1.12	1.17	1.56	1.71
benzo[*k*]fluoranthene	0.88	1.28	2.24	2.25
benzo[*a*]pyrene	0.92	1.61	1.58	1.58
dibenz[*a,h*]anthracene	0.97	1.65	0.96	0.93
benzo[*ghi*]perylene	1.03	1.04	1.15	1.26
indeno[1,2,3-*cd*]pyrene	1.06	1.05	1.26	1.46

[a] Data normalized to results at 500 psi.

Pressure Effect. We investigated the effects of changing the pressure and temperature on the extraction efficiency. Obviously, a certain amount of pressure is needed to maintain the solvents as liquids at or above their atmospheric boiling points. These pressures need not be excessive, however. For example, 5 atm (73.5 psi) is all that is needed to keep acetone (atmospheric bp 56.3 °C) liquid at 100 °C. The effect of pressure on recoveries of analytes was investigated by extracting silica loaded with PAHs at pressures ranging from 500 to 2500 psi, as described in the Experimental Section.

With the dry silicas, no trend was seen with respect to pressure effects on recoveries of the PAHs. However, a trend was seen with the wet silicas with 300 Å pore material. As can be seen in Table 2, 1500, 2000, and 2500 psi pressures show improved recovery over the use of lower pressures. The improved recovery is seen starting with fluoranthene and is most pronounced up to dibenz[*a,h*]anthracene, although improvement is also seen with benzo[*ghi*]perylene and indeno[1,2,3-*cd*]pyrene at 2000 and 2500 psi.

These data confirm the hypothesis that the increased pressures and temperatures used in the ASE process will allow analytes that are found in pores effectively blocked by water to be more rapidly extracted than is possible at room temperature and atmospheric pressure. Elevated pressure will force the solvent into these pores. The increased solubility of water in organic solvents that occurs at elevated temperatures increases the contact of the solvent with the analytes, and these "trapped" analytes are extracted more quickly.

In addition to providing improved recoveries, operating at higher pressures does have a practical aspect. Cells can be filled with solvent much more quickly at high pressure, >1500 psi, especially when extracting samples having small particles, such as sediment samples.

Table 3. Effect of Temperature on the Recovery of TPHs from Soil Using ASE (1200 mg/kg Certified Value)

temp (°C)	amount found (mg/kg, $n = 5$)	RSD (%)
27	974	6.0
50	1118	5.0
75	1190	2.0
100	1232	1.0

Table 4. Effect of Temperature on the Amount Extracted from Chattanooga Shale

extraction temp (°C)	normalized area from GC	absorbance ($\times 10^2$ AU) at 600 nm
50	1170	0.0
100	2552	1.35
150	3092	4.85
200	3500	15.0

Temperature Effect. One would expect the temperature to have a pronounced effect on the performance of ASE from the standpoint of solubility and mass transfer. We studied the effect of temperature on the recovery of TPHs using the following conditions for the extractions: preheat method, PERC as the extraction solvent, 2500 psi, 5 min static after equilibration, 3-g soil samples, 3.5-mL cell volume, and 4.5−5.0 mL of solvent used for each extraction. The oven temperature was varied from room temperature (27 °C) to 100 °C in the different experiments. The results of these tests are given in Table 3. An increase in temperature (above 50°C) gives improved precision (relative standard deviation, RSD) and improved recovery.

Another set of experiments was performed to investigate the effect of temperature on extraction. Ten-gram samples of Chattanooga shale were extracted with toluene at 50, 100, 150, and 200 °C and 2000 psi using a preheat method. The results (Table 4) show that, with increasing temperature, an increasing amount of material is extracted. The amount extracted at 100 °C is the same as obtained with 4 h of automated Soxhlet extraction with toluene.

Prefill and Preheat. The preheat method seemed to work well for samples containing less volatile components; however, loss of more volatile compounds occurred when this method was used. For example, the recovery of naphthalene was 50−70% when the preheat method was used, and the recovery of chlorinated pesticides (endrin, heptachlor, DDT, etc.) was in the same range. The prefill method was developed in an effort to prevent the loss of the volatile compounds. The intent was that, if the solvent were introduced first followed by heating the sample, then the volatile compounds would be trapped in the solvent and not lost during the cell heat-up, as was seen with the preheat method.

Experiments were performed to investigate the recovery of more volatile compounds by spiking a standard mixture on clean sand in an extraction cell. Methylene chloride was the solvent, the cell temperature was 60 °C, and 5-min equilibration and 5-min static method steps were used with the pressure at 2500 psi. Four extractions were performed, and duplicate injections were made (see Table 5 for the results). Good recoveries for all compounds, even the more volatile BTEX compounds (benzene, toluene, ethylbenzene, and xylene) were obtained. Under the same

Table 5. Recovery by ASE of Volatile Compounds Spiked on Sand

compound	av recovery (%), $n = 4$	RSD (%)
benzene	99.7	2.5
toluene	99.5	2.7
ethylbenzene	100	3.7
o-xylene	99.6	1.2
n-nonane	97.1	2.6
n-decane	98.1	1.0
n-undecane	99.5	0.9
naphthalene	99.9	1.7
2-methylnaphthalene	99.4	2.3
n-tetradecane	99.0	2.2
n-pentadecane	97.2	3.0

Table 6. Effect of Sample Size on TPH Recovery (1200 or 2060 mg/kg Certified Value, $n = 3$ for Each)

sample wt (g)	cell size (mL)	solvent vol (mL)	recovery (%)	RSD (%)
3.5	3.5	5	103	2.0
8.0	7.0	9	107	2.1
12	10.0	13	105	1.8
16	16.0	20	110	2.0

Table 7. Recovery of PCBs from Sewage Sludge[a]

PCB congener	av recovery (%), $n = 6$	RSD (%)
PCB 28	118	2.5
PCB 52	114	4.7
PCB 101	143	7.4
PCB 153	110	5.8
PCB 138	110	3.9
PCB 180	160	7.5

[a] Analyte concentration range: 160−200 μg kg^{-1} component.

Table 8. Recovery of PCBs from Oyster Tissue[a]

PCB congener	av recovery (%), $n = 6$	RSD (%)
PCB 28	90.0	7.8
PCB 52	86.9	4.0
PCB 101	86.3	1.5
PCB 153	88.5	3.5
PCB 138	86.9	3.0
PCB 180	87.0	4.3

[a] Analyte concentration range: 50−150 μg kg^{-1} component^{-1}.

conditions, the recovery of pentane (bp 36 °C) was 90.1% with 1.8% RSD. Based on these results and additional work that showed no difference in the recovery of "less volatile" compounds, the prefill method appears to be the preferred mode of operation for ASE, and it was used for all subsequent experiments.

Solvent Volume. Another experimental parameter investigated was the amount of solvent necessary to obtain complete extraction. Samples of the ERA TPH soil were used. Sample sizes from 3.5 to 16 g were used with cells ranging from 3.5 to 16 mL. The TPH recovery was determined for the ERA soil using the IR method outlined in the Experimental Section. The temperature was 100 °C, the preheat and prefill techniques were used, and the pressure was 2000 psi. The data from these series of experiments are shown in Table 6. The amount of solvent needed to achieve quantitative extraction of the TPH can be expressed as 1.2−1.5 times the volume of the empty extraction cell used to contain the sample. In other words, a volume of 12−15 mL of solvent is needed to achieve complete extraction from a cell with a 10-mL volume.

Additional work with samples ranging from 1 to 30 g of heavily contaminated soil (SRS103-100, which is ∼11 wt % organic extractable), with cells ranging in volume from 3.5 to 32 mL, confirmed that the same ratio of sample cell volume to the volume of solvent also holds for heavily loaded samples. Quantitative recovery of the PAH in this sample, compared to the certified values, was obtained in these experiments. The authors used the same ratio for all samples investigated for this study and in work demonstrating the equivalency of ASE to Soxhlet and automated Soxhlet extraction.[25,26]

Thermal Degradation. Since extractions are done at elevated temperatures, thermal degradation is a potential concern. The degradation of DDT and endrin during GC analysis is used as an indication of active sites or excessive thermal conditions.[27] DDT breaks down to DDD and DDE, and endrin forms endrin aldehyde and endrin ketone. These same compounds were used to determine if thermal decomposition occurs during ASE. In separate experiments, DDT and endrin were spiked on sand at the 5 μg/kg (ppb) level. The spiked sand samples were extracted at 150 °C (normal extraction temperature for these compounds is 100 °C), and the extracts were analyzed by GC with ECD. Dieldrin was added to the collection vials as an internal standard, and the volumes were reduced to 1 mL with a nitrogen gas stream before analysis. The average recoveries were 103% with 3.9% RSD for DDT and 101% with 2.4% RSD for endrin with three extractions and duplicate injections of each. There was no evidence of the presence of DDE or DDD in the experiments with DDT, and neither endrin aldehyde nor endrin ketone was observed in the experiments with endrin. The minimum detectable quantity for these analytes was 0.015 pg on-column, corresponding to <0.5% of the original levels spiked on the sand.

Certified Samples. Following the above studies of the operational parameters, additional experiments were conducted to determine the recovery of PCB from a sewage sludge sample using the following conditions: prefill method, 100 °C, hexane/acetone (1:1), 5-min equilibration, 5-min static time, 18-mL final volume, 2000 psi, and 10-g samples. These extracts were cleaned up before analysis by passing them through glass columns containing silver nitrate/sulfuric acid-loaded silica gel, followed by concentration to 1 mL. The results from these extractions are shown in Table 7. The recovery is based on the results by Soxhlet extraction of the same samples. The Soxhlet extraction was done with hexane for 6 h with 3-g samples.

The oyster tissue samples were extracted under the following conditions: prefill method, 100 °C, isooctane, 5-min equilibration, 5-min static time, 18-mL final volume, 2000 psi, and 5-g samples. The sample extracts were concentrated to 5 mL prior to analysis,

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Table 9. Recovery of PAHs from Urban Dust (SRM 1649)[a]

compound	av recovery (%), $n = 6$	RSD (%)
phenanthrene[b]	113	2.0
fluoranthene[c]	88.5	5.2
pyrene[b]	91.0	5.9
benz[*a*]anthracene[c]	97.2	5.7
chrysene[b]	101	4.2
benzo[*b*]fluoranthene[b]	115	6.2
benzo[*k*]fluoranthene[b]	112	6.7
benzo[*a*]pyrene[c]	125	6.2
benzo[*ghi*]perylene[c]	108	5.8
indeno[1,2,3-*cd*]pyrene[c]	108	6.7

[a] Analyte concentration range: 1−7 mg kg^{-1} $component^{-1}$. [b] Compounds with noncertified values. [c] Compounds with certified values.

and no clean-up was performed on the extracts. Table 8 shows the results of these extractions.

Table 9 shows the results of the extractions of SRM 1649, urban dust. The following conditions were used for these extractions: prefill method, 100 °C, methylene chloride/acetone (1:1 v/v), 5-min equilibration, 5-min static time, 18-mL final volume, 2000 psi, and 10-g samples. These results also show that quantitative results can be achieved for PAHs using ASE.

The Canadian marine sediment samples were extracted using the following conditions: prefill method, acetone/methylene chloride (1:1) as the extraction fluid, at a pressure of 2000 psi and a temperature of 100 °C, 5-min equilibration, 5-min static, and 18-mL final volume. Sample weights of 5 g were used. The extracts were treated with copper amalgam to remove sulfur and then concentrated to 5 mL prior to analysis. The results are shown in Table 10. Only four of the compounds were outside the 90% confidence interval (CI) for the certified values: anthracene, benzo[*b*]fluoranthene, benzo[*k*]fluoranthene, and dibenz[*a*,*h*]anthracene. The average recovery for anthracene was lower than the certified value, while the results for the other three compounds were higher than the certified values. It is interesting to note that benzo[*b*]fluoranthene and benzo[*k*]fluoranthene were two of the compounds that demonstrated the largest changes in recovery with pressure in the pressure effect experiments reported earlier.

Table 10. Recovery of PAHs from Marine Sediment HS-3 (mg/kg)

compound	av recovery $n = 4$	90% CI[a]	CV[b]	90% CI[a]
naphthalene	8.87	1.00	9.00	0.70
acenaphthylene	nd[c]	na[d]	0.30	0.10
acenaphthene	4.89	0.51	4.50	1.50
fluorene	10.9	1.26	13.6	3.10
phenanthrene	68.8	6.44	85.0	20.00
anthracene	7.73	0.57	13.4	0.50
fluoranthene	54.7	4.82	60.0	9.00
pyrene	33.7	2.83	39.0	9.00
benz[*a*]anthracene	12.8	1.07	14.6	2.00
chrysene	15.0	1.52	14.1	2.00
benzo[*a*]pyrene	6.27	0.65	7.40	3.60
benzo[*b*]fluoranthene	11.5	1.27	7.70	1.20
benzo[*k*]fluoranthene	10.2	1.28	2.80	2.00
benzo[*ghi*]perylene	4.14	0.69	5.00	2.00
dibenz[*a*,*h*]anthracene	2.58	0.33	1.30	0.50
indeno[1,2,3-*cd*]pyrene	4.30	0.77	5.40	1.30

[a] Confidence interval of the mean. [b] Certified value. [c] Not detected at the level of detection (1.5 mg/kg). [d] Not applicable

Extractions were performed to determine the reproducibility of ASE when doing multiple samples. The ERA soil was chosen, and the TPH content was determined. Eighty-five samples in the 4−8-g range were extracted sequentially and analyzed by IR. The average recovery was 103% with 2.7% RSD.

CONCLUSIONS

The data presented strongly indicate that, by using elevated temperatures and pressures with organic solvents, we can achieve an enhanced extraction of analytes from solid samples. Accelerated solvent extraction (ASE) gives recoveries comparable to those obtained with Soxhlet and other techniques in use while spending only a fraction of the time and solvents needed for those techniques. ASE shows good potential for the recovery of volatile as well as semivolatile compounds.

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