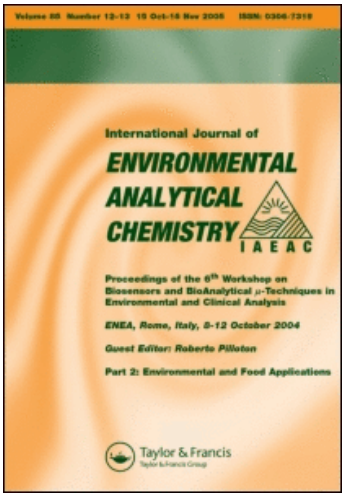

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SCREENING METHODOLOGY FOR COAL-DERIVED ORGANIC CONTAMINANTS IN WATER

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A screening methodology designed to detect the presence of organic materials that leach into water from coal deposits was developed and evaluated. Analytical objectives included the ability to detect 16 polynuclear aromatic hydrocarbons (PAHs) at the lowest practical levels, capability for fingerprint analysis of other compounds, and ease of use under remote field conditions. The approach developed involved drawing 1 L water samples through a styrene divinylbenzene-based solid-phase extraction cartridge by suction, elution of the cartridge with tetrahydrofuran/hexane, evaporative concentration of the eluent, and reconstitution in acetonitrile, followed by analysis using high-pressure liquid chromatography with ultraviolet absorption and fluorescence detectors. The method was found to be easy to use under field conditions, providing generally acceptable recoveries and, in most cases, lower detection limits than current regulatory methods. The ability to detect PAHs and other organic compounds in simulated coal leachate solutions was demonstrated.

Keywords: Polynuclear aromatic hydrocarbons (PAHs); Coal; Leachate; Water analysis; High-pressure liquid chromatography (HPLC); Solid-phase extraction (SPE); Hydrophobic organic contaminants (HOC)

INTRODUCTION

Coals contain numerous organic compounds that are toxic, including known and suspected carcinogens classified as polynuclear aromatic hydrocarbons (PAHs). It has been suggested that water contacting coal deposits can be become contaminated, as these materials dissolve at trace levels [1,2]. Owing to their lower state of digenesis, and the resulting abundance of low molecular weight compounds and polar functional groups, it has been proposed that lignite coals would most readily leach PAHs, phenols, and other organic compounds that might pose health risks [3].

Several PAHs are known to be carcinogenic in laboratory animals, increasing the incidence of skin, lung, liver, and stomach cancer, as well as injection-site sarcomas. Additionally, most of the carcinogenic PAHs have also been found to be mutagenic [4]. Epidemiological studies on laboratory animals have shown an increase in skin,

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lung, bladder, and gastrointestinal cancers resulting from dermal contact, inhalation, and ingestion of PAHs [5]. The primary organs that PAHs affect contain actively proliferating cells, and include the intestinal epithelium, bone marrow, lymphoid organs, and testes [6]. Benzo-[*a*]-pyrene (BaP), considered the most carcinogenic of the PAHs, is suspected of being the primary cause of skin cancer in chimney sweeps in the 1770s [7]. It has been hypothesized that long-term exposure to PAHs and other organic chemicals might be the cause of Balkan Endemic Nephropathy (BEN), a kidney disease found in rural regions of Bulgaria, Romania, Serbia, and Croatia. Laboratory leaching of coal samples from the region yielded soluble organic matter containing large amounts of aromatic structures, suggesting the possibility of PAHs [8]. The difficulty in collecting and analyzing an adequate number of water samples from these very remote locations has been a significant limitation in further testing this hypothesis.

Because PAHs have such high levels of carcinogenic and mutagenic activity, the possibility of their presence in water supplies has long been a concern in drinking water regulation. The U.S. EPA lists 16 PAHs and the European Union lists 6 as "priority pollutants," for which special attention is to be given in research, monitoring, and regulatory programs. In 1984, BaP was given a guideline value for drinking water of 0.7 μg/L by the World Health Organization and the U.S. EPA sets a Maximum Contaminant Level for drinking water supplies at 0.2 μg/L [9,10]. Concentrations of PAHs in drinking water supplies have been monitored throughout the world and are generally found to be in the low nanogram per liter range [11–15], with slightly higher concentrations, the low microgram per liter range, described in some surface waters [6,13].

The leaching potential of PAHs depends primarily on aqueous solubility, which for the 16 priority PAHs range from 32 mg/L for naphthalene (NAPH) to 1.5 μg/L for BaP [16]. Concentrations of PAHs in surface water are typically higher than those found in groundwater because of increased levels of colloidal material and dissolved organic matter (DOM), which serve to sorb or bind hydrophobic materials, resulting in an apparent increase in solubility. This same phenomenon reduces groundwater concentrations, as sorption to organic matter in aquifer solids along the flow path will very effectively remove PAHs. However, DOM has been shown to alter PAH mobility [17] and colloid-facilitated transport of hydrophobic organic contaminants (HOCs) in groundwater has also been demonstrated [18]. Thus, PAH contamination of groundwater can be hypothesized to be most likely in shallow water supplies in regions with thin soils, where DOM and colloid levels are high and contact with organic-rich soil is low. Even in these situations concentrations are likely to be low, and any sampling and analysis scheme must be capable of achieving very low detection limits.

Several studies have investigated the leaching of acidity, metals, and other ions from coal [19–22] but organic compounds have received only limited attention. Most of the previous work on leaching of organic compounds has focused on PAHs. The reported analytical techniques include: gas chromatography (GC) with mass spectrometry (MS) or flame ionization detection (FID); high-pressure liquid chromatography (HPLC) with ultraviolet (UV), fluorescence (Fl), or MS detection; and supercritical fluid chromatography (SFC) with UV or MS detection. Of these, HPLC with UV or Fl detection, and GC with FID or MS detection, are the most common [13,23].

Because of the low solubility of many HOCs, particularly PAHs, additional analytical techniques are required to achieve method detection limits that are useful for the

concentrations found in environmental samples. The primary approach used to achieve low detection limits involves selective extraction, to isolate the target analytes from interfering compounds, and sample concentration. Closed-loop stripping and liquid–liquid extraction with evaporative concentration have been widely used, but solid-phase extraction (SPE) has become increasingly common since it was first demonstrated for PAHs in surface water samples [24]. Since then, the use of SPE has increased and its effectiveness has been verified [25,26]. This procedure forms the basis for U.S. EPA drinking water method 550.1 and several proposed modifications [27–29]. These methodologies are designed as laboratory procedures, so either large volume samples (typically 1 L or more) must be transported to the laboratory, or the SPE procedure (which typically includes conditioning and wetting steps) must be adapted to field conditions. These approaches may present logistical difficulties.

Many different commercially available SPE columns for PAH extraction currently exist. Toribio *et al.* [25] investigated the use of various conditioned SPE cartridges with packed-column SFC for 35 common contaminants including pesticides, PAHs, and phenols. They found that a styrene divinylbenzene cartridge (Isolute® ENV+ SPE) provided some of the best recoveries available, ranging from 34.6 to 105%. Castillo *et al.* [30] reported on the stability of phenolic compounds extracted with Isolute® ENV+ cartridges. They found losses of less than 25% for compounds with log octanol–water partition coefficients greater than 2 after one month of storage at room temperature. Neither of these studies addressed issues related to field sampling and the use of HPLC analysis. The manufacturer makes a number of additional claims for this SPE cartridge including (1) elimination of the need for solvent pretreatment, (2) high flow capacity, and (3) effectiveness in concentrating other materials that are likely to leach from coal, such as phenolic and amino compounds [31]. To our knowledge, these claims have not been independently verified.

The objective of this study was to develop a screening methodology that could be used in remote locations for the presence of coal-derived compounds in drinking water at the lowest practical detection limits. The Isolute® ENV+ SPE cartridge was selected because of its high capacity and the claim that solvent preconditioning was not necessary. The sampling apparatus developed for this method requires only battery power and can operate hands-free once a sample has been collected. Owing to the positioning of a peristaltic pump after the SPE cartridge, water samples come into contact with only the glass separatory funnel before HOCs are isolated and then only the loaded cartridges require transport from the field site to the lab where they can be analyzed. HPLC was used for separation because it is applicable to compounds with a wide range of molecular weights, volatilities, and solubilities. Both fluorescence and UV detection were used in order to take advantage of the very low detection limits of fluorescence, particularly for most of the PAHs, and the broad range of unsaturated and aromatic compounds that can be detected by UV. Although LC/MS offers an additional level of chemical specificity and potential compound verification, it has other less desirable properties, making it unattractive for use in screening methods. For compound confirmation, fragmentation patterns are required and PAHs exhibit very few fragment ions, if any [32]. Furthermore, MS detectors used on LC systems have limits of detection down to 1 pg, at best [33]. Even using a microbore LC column with a 1μL injection volume, method detection limits would be roughly 1 μg/L, assuming the method is ideal (i.e., perfect recovery, no chromatographic peak broadening) with a 1000-fold concentration step utilizing SPE. The detection limit

desired for this screening method for detecting PAHs in drinking water still requires a detection limit three orders of magnitude lower, in the nanogram per liter range. The developed method was evaluated for the ability to detect the 16 priority pollutant PAHs, and to respond to other unidentified compounds leached from coal samples.

EXPERIMENTAL

Water samples were collected in 1L glass bottles and transferred to 1L separatory funnels onto which Isolute® ENV+ cartridges had been attached using a Teflon™ tape "gasket" as shown in Fig. 1. No pretreatment or interference elutions was used with the cartridges. Samples were drawn through the cartridge by suction at a rate of approximately 15 mL/min using a peristaltic pump attached to the effluent end of the cartridge. By the use of an airtight seal, the water sample loading to the cartridge during SPE was maintained at a level below the gasket to prevent losses of HOCs to the Teflon™ tape. Following the concentration procedure, cartridges were loosely double wrapped in aluminum foil and allowed to air dry for several days at ambient temperature.

After drying, cartridges were eluted with 1.5 mL of a tetrahydrofuran (THF)/hexane (HEX) mixture (50 : 50 v/v) using vacuum filtration. A 5-min soak step was performed with the first 0.5 mL of eluent, with a small amount of additional solvent used when necessary to prevent drying. The remaining solvent was then passed through the cartridge. The eluted sample was reduced by evaporation under a gentle airflow until nearly all of the solvent was removed. The residue was then reconstituted in acetonitrile to a final volume of 1 mL.

A Perkin-Elmer HPLC system utilizing a series 200 LC pump fitted with a 200 µL sampling loop and a Supelco LC-PAH column (5 µm particle size, 25 cm length × 4.6 mm ID) without temperature control was used to separate constituents. Sequential detection was employed using a Waters 2487-dual wavelength absorbance detector and

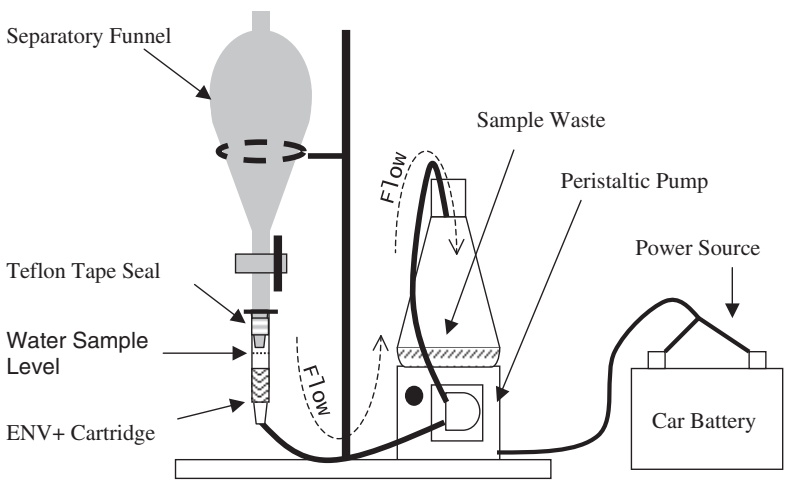
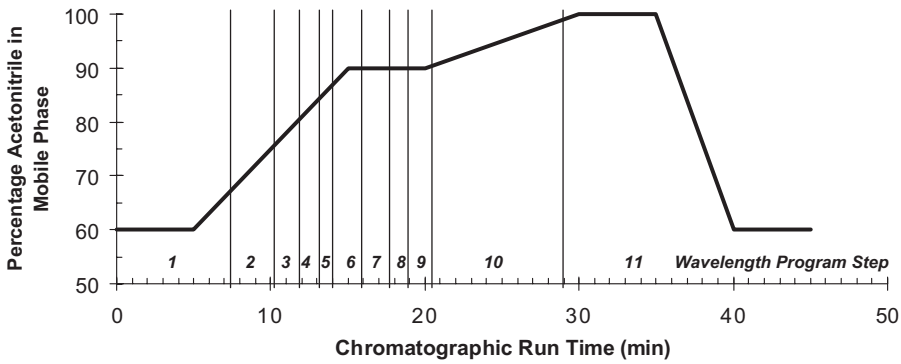


FIGURE 1 Field transportable SPE extraction apparatus.



Wavelength Program Step	Excitation Wavelength	Emission Wavelength	Gain	Peaks eluted during wavelength step
1	280	340	1000	NAPH
2	270	323	100	ACY*, ACE, FLU
3	249	362	1000	PHEN
4	250	400	1000	ANTH
5	285	450	1000	FLT
6	333	390	1000	PYR
7	285	385	1000	BaA
8	263	358	1000	CHRY
9	295	420	1000	BbF
10	296	405	1000	BkF, BaP, DIBahA, BghiP
11	300	500	1000	INPY

* Acenaphthylene is not detectable using fluorescence detection.

FIGURE 2 Gradient elution and wavelength programs developed for HPLC separation. Gradient elution program was performed with a constant flow rate of 1.5 mL/min. Wavelength program has been optimized (11-step program) for the detection of 15 of the 16 EPA priority PAHs using fluorescence detection.

a Waters 474-scanning fluorescence detector. Acetonitrile and water were used as the mobile phase in the gradient elution program shown in Fig. 2. The 11-step wavelength program, also shown in Fig. 2, was developed for the fluorescence detector to achieve the best possible detection limits for 15 of the 16 PAHs, based on previous reports in the literature [27,34–38]. Because the fluorescence spectrum for acenaphthylene (ACY) is virtually nonexistent, UV detection (254 nm) was used to analyze for this compound. This was selected in part because most aromatic and unsaturated compounds will absorb light at this wavelength thus allowing the UV scan also to be used as a means of observing other organic compounds in the sample [38,39].

Method detection limits and analytical recoveries were determined using a mixed analytical standard in acetonitrile/methanol (90 : 10 v/v) (Supelco) containing the 16 EPA priority PAHs: naphthalene (NAPH), acenaphthylene (ACY), acenaphthene (ACE), fluorene (FLU), phenanthrene (PHEN), anthracene (ANTH), fluoranthene (FLT), pyrene (PYR), benz[*a*]anthracene (BaA), chrysene (CHRY), benzo[*b*]fluoranthene (BbF), benzo[*k*]fluoranthene (BkF), benzo[*a*]pyrene (BaP), dibenz[*a*,*h*]anthracene (DIBahA), benzo[*g*,*h*,*i*]perylene (BghiP), indeno(1,2,3-*c*,*d*)pyrene (INPY). Aliquots of the standard were spiked directly into 1 L water samples in the separatory funnel prior to concentration on the SPE cartridges. Detection limits were estimated using

the calibration-design-dependent method based on 3–6 points, depending on individual compound response [40]. This method utilizes multiple standards with various concentrations near the detection limit to create a least squares regression fit for a calibration curve and bases the limit of detection on the confidence intervals about this regression [39]. Standards used for determining the calibration curve and detection limit were subjected to the complete analytical method, ensuring that losses during analysis or due to recovery problems were taken into account. Some of the R^2 values for the calibration curves were low, perhaps reflecting some of the problems observed with recovery percentages. Overall recoveries were calculated as the fraction of the mass recovered using a calibration curve produced from dilutions of the same standards. Recoveries for the 16 PAHs were determined and found to range between 15 and 83% depending on the compound.

Leachate solutions were prepared from three coal samples: Low Grade Coal (collected from a surface mine in western Bulgaria), Lignite Coal (coal consumed in the Vratza district of Bulgaria and reported to be from Ukrainia), and High Grade Coal (Michigan State University's power plant supply; blend of Virginia, Ohio, and North Carolina coals). Dry coal samples were crushed and placed into 1 L of ultrapure water (>16 MOhm cm) in 1 L glass bottles, then shaken for approximately two weeks on an orbital agitator. The pH of the coal samples in water averaged 6.2. After shaking, solutions were centrifuged in glass centrifuge tubes (11,952 RCF), passed through 47 mm type AE glass-fiber filters (nominal pore size 1 μm) under vacuum, and then loaded onto the SPE cartridges. This procedure was designed to ensure that aqueous solutions would contain only dissolved PAHs or those bound to particles smaller than 1 μm. All glassware used in this procedure was cleaned using soap and water, followed by 3 hexane rinses, one acetone rinse and oven drying at 105 °C for 60 min or more.

RESULTS AND DISCUSSION

The SPE extraction apparatus was relatively sturdy and compact, and with the use of a 12 volt pump it was found to work well inside a field-sampling vehicle without external power. Loading of the cartridges was relatively simple and hands-free once the separatory funnel assembly was set up. Clogging of the cartridge was never observed and maintaining the desired flow rate (~15 mL/min) was not problematic for either the spiked waters or the coal leachate solutions. The cartridges proved easy to elute, concentrate, and prepare for HPLC separation and UV/fluorescence detection. The cartridge manufacturer's claims of ease of use, that solvent pretreatment is not necessary, and the ability to load the cartridges at relatively high flow rates, were confirmed. Claims as to the effectiveness of the cartridges in concentrating other materials such as phenolic and amino compounds were not evaluated. Sample preparation in the laboratory required little time (less then 30 min for 12 samples). Chromatographic analysis required 45 min run times, but this was not a problem because the HPLC was automated.

Recovery efficiencies and method detection limits for the 16 PAHs from spiked water samples are reported in Table I. Recovery was greatest for the two- and three-ringed PAHs, and averaged 50% for all compounds. Low recoveries were found for some of the four- and five-ringed compounds: BaA (22%), CHRY (15%), and DIBahA

TABLE I Method recovery and estimated detection limits for PAHs

Peak number	*Chemical*	*Average recovery*	*Relative std. dev.* (%)	*Method DL* (μg/L)	*Confidence level* (%)	R^2	*Method DL U.S. EPA 550.1* (μg/L)
1	NAPH	0.43	26	0.002	95	0.9997	2.2
2	ACY	0.73	14	0.050	95	0.9994	1.41
3	ACE	0.80	15	0.69	95	0.7121	2.04
4	FLU	0.83	15	0.004	95	0.9946	0.126
5	PHEN	0.75	12	0.012	95	0.8974	0.15
6	ANTH	0.55	12	0.002	95	0.6940	0.14
7	FLT	0.46	16	0.004	95	0.9698	0.009
8	PYR	0.37	15	0.024	86	0.8224	0.126
9	BaA	0.22	34	0.012	95	0.8464	0.004
10	CHRY	0.15	36	0.081	93	0.7466	0.16
11	BbF	0.49	9	0.001	95	0.9951	0.006
12	BkF	0.50	29	0.001	95	0.9955	0.003
13	BaP	0.44	24	0.002	95	0.9940	0.016
14	DIBahA	0.20	51	0.017	95	0.9728	0.035
15	BghiP	0.50	20	0.005	95	0.9794	0.02
16	INPY	0.55	34	0.15	95	0.9778	0.036

(20%). Toribio *et al*. [25] also reported low recoveries for two of these compounds (BaA and CHRY) and speculated that this was due to incomplete elution from the cartridges. Overall, recoveries were somewhat lower than are observed for regulatory methods such as U.S. EPA method 550.1 [29], but were considered acceptable for screening purposes. The low molecular weight compounds (NAPH, ACY, ACE, FLU, and PHEN) had comparable or better recoveries than methods involving preconditioning and cleaning steps [25,41]. Because the low molecular weight compounds are more likely to leach from coal deposits, this selectivity was considered desirable for the analytical objectives of the present study.

It must be kept in mind that chromatographic methods alone cannot confirm the presence of specific compounds, so the occurrence of corresponding peaks in the standard and coal leachate samples indicate only the possible presence of the PAH compound. The absence of a peak, however, does confirm that the corresponding PAH is not present, and this was the primary objective in developing this screening method. When corresponding peaks are found, they can be quantified to determine the maximum possible concentration, assuming that the peak is due entirely to the corresponding PAH. Again, this is appropriate for screening methodologies that commonly seek to establish that concentrations are below some regulatory level of concern.

Fluorescence and UV chromatograms for the three coal samples are shown in the bottom three panels of Figs. 3 and 4. The top panels of Figs. 3 and 4 show the fluorescence and UV chromatograms, respectively, for the PAH spiked samples. At least one potential PAH was found in each leachate sample and maximum possible PAH concentrations are reported in Table I. The maximum possible concentrations of PAHs observed ranged from 4 ng/L BkF and BaP to 0.78 μg/L ACE. Naphthalene was detected but quantification was not possible owing to other chemical interferences. In addition to 15 of the EPA priority PAHs detectable using fluorescence, other unknown peaks were observed in the fluorescence chromatograms.

As peaks corresponding to PAHs were found in all of the tests, we conclude that dissolved PAHs can be detected in water contacting coal using the methodology

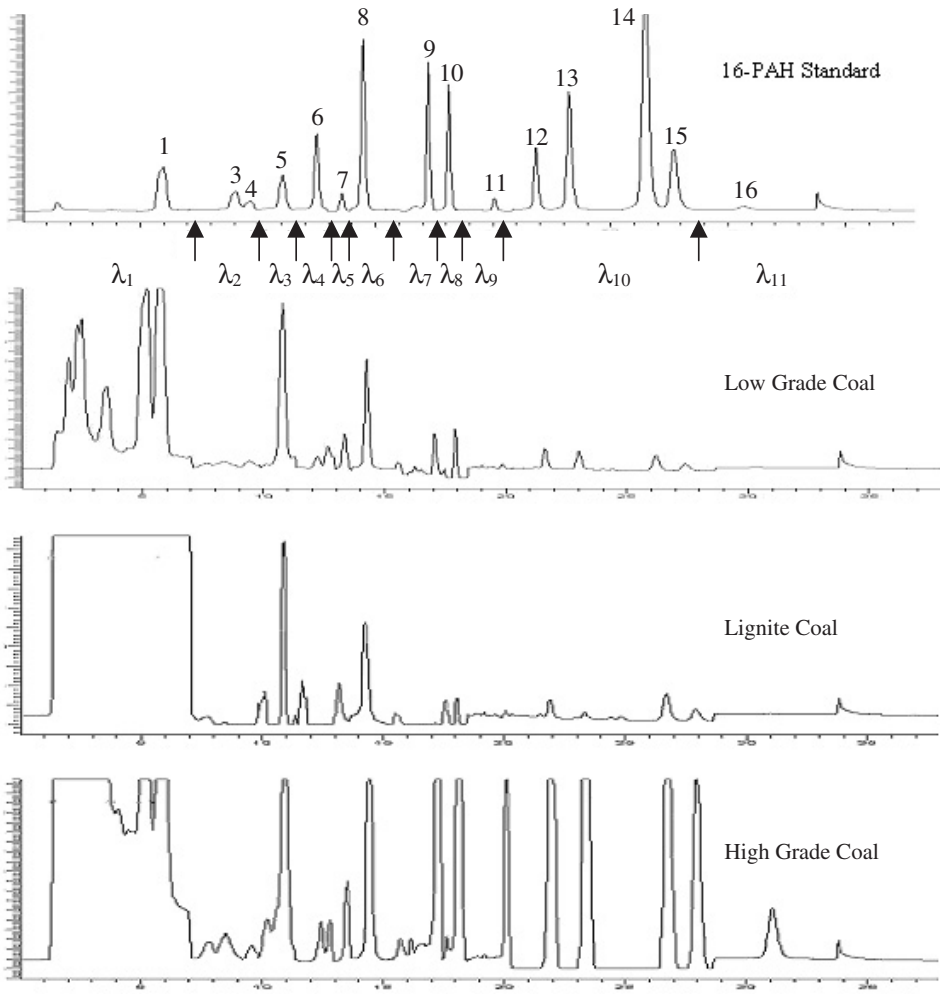


FIGURE 3 Chromatograms produced from wavelength-programmed fluorescence detection. The top chromatogram was produced using a 16-PAH standard in the low microgram per liter range (5.0 μg/L NAPH). Arrows denote changes in wavelength; corresponding wavelength and PAH peak numbers are also shown. The bottom three chromatograms show the results of coal leaching in water.

reported here. It should be noted, however, that maximum concentrations were low – less than 1 μg/L in all cases. The only compound that is regulated in the U.S., BaP, was present at a concentration approximately two orders of magnitude below the regulatory level. However, these results cannot be used directly to estimate the exposure that might occur under field conditions. These tests used distilled water and only a two-week contact time. This might result in lower values than would be found under field conditions with long groundwater residence times and water containing dissolved organic material. However, higher levels might be expected in the laboratory tests because of the vigorous mixing conditions employed and the large amount of organic material that dissolved from the coal samples themselves. The extent of dilution by water not contacting coal is also difficult to predict, as this would be highly site specific. Nonetheless, the methodology developed clearly does have the ability to detect PAHs at

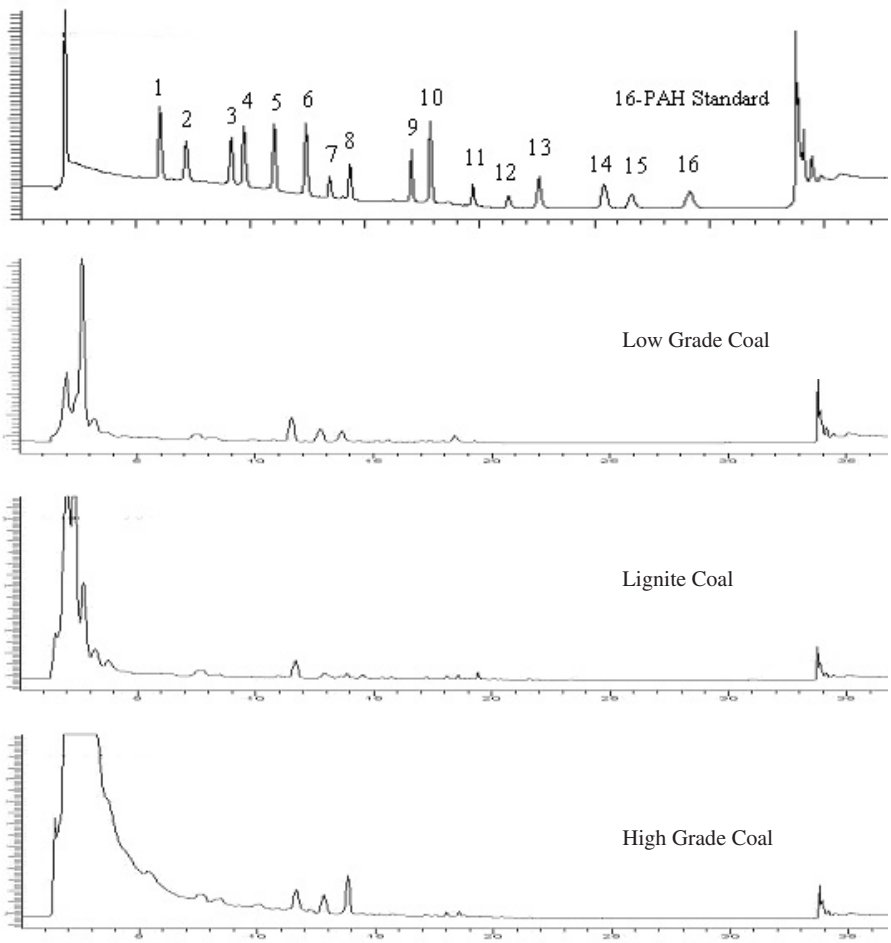


FIGURE 4 Chromatograms showing the use of fixed-wavelength (254 nm) UV detection. The top chromatogram was produced using a 16-PAH standard in the low milligram per liter range (5.0 mg/L NAPH). The bottom three chromatograms show the results of coal leaching in water.

levels well below those that are regulated, and below or similar to those achievable by U.S. EPA method 550.1 [29].

The fluorescence and UV chromatograms were both also used as a form of "fingerprint analysis" in which characteristic peaks can be used to qualitatively evaluate the similarity or dissimilarity of samples. Both Bulgarian lignite and MSU coal samples showed a significant number of unknown fluorescent and ultraviolet peaks, mostly before naphthalene detection. These early eluting compounds represent more soluble constituents of the coals, but are clearly not PAHs. These peaks create problems when attempting to quantify naphthalene from fluorescence chromatograms. Therefore the UV detection of naphthalene was also employed. Unfortunately, this approach was not always successful, as shown in Fig. 3, since the concentration was often below the UV detection limit (0.2 μg/L). Additional clean-up of samples would thus be warranted if more precise quantification of naphthalene were required. Although the chemicals responsible for the other peaks were not identified or quantified, their

presence suggests that there are many other HOCs for which this method can be utilized. By using sequential detection, this method effectively analyzes for individual PAHs using fluorescence detection while UV detection is less specific and monitors for a number of other organic compounds.

One source of interference noted during method development was changes in the fluorescence and UV signals due to the increased concentration of acetonitrile present in the mobile phase. As the percentage of acetonitrile increased, baselines increased resulting in a decreased range of detection, even with high-purity acetonitrile. These problems were overcome in fluorescence detection during wavelength programming by zeroing the detector after each wavelength shift. These changes in the fluorescence wavelength during chromatographic runs resulted in disturbed baselines that were later removed by subtracting blank samples (although some baseline disturbance is still visible in Fig. 4).

Even more compounds could potentially be identified using this method by additional wavelength programming with either detector. However, each time a wavelength shift is incorporated into the analytical method, a significant window of the chromatogram without peak detection must be allowed for the detector to stabilize. As the number of wavelength changes increases, a longer chromatographic run time is necessary. For this reason, the improvements from refining wavelengths must be weighed against the desired time of analysis. With the current set-up, an 11-step wavelength program resulted in the identification of the 16 EPA priority PAHs.

CONCLUSION

This method is capable of screening water contaminated by coal leachate for the 16 EPA priority PAHs at detection limits lower than or similar to accepted methodologies. Peaks corresponding to all but one of the PAHs were found in three coal leachate samples. The maximum possible concentrations varied and not all PAHs were found in each sample. The sampling methodology can be readily employed in the field using a simple extraction apparatus. The presence of other organic compounds was also observable, although no attempt was made in this study to identify or quantify these compounds. This information could be used as a ''fingerprint technique'' to characterize similarities and differences between the HOCs in different samples. Once compounds are observed, more time-consuming and labor-intensive analytical methods could be employed for accurate qualification and quantification. However, this method is capable of verifying that concentrations for the 16 priority pollutant PAHs are below some specified level of concern. This capability makes it an effective screening tool that can be used to evaluate whether drinking water in remote locations has been contaminated by coal.

Acknowledgments

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