Rapid Analysis of PAHs in Fly Ash Using Thermal Desorption and Fast GC–TOF-MS

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Abstract

Polycyclic aromatic hydrocarbons (PAHs) are semivolatile organic compounds that may form as a result of incomplete combustion of organic materials. After they are produced in combustion systems, this class of chemicals can be emitted with flue gas or adsorbed in combustion residues such as fly ash and bed ash. The purpose of this study is to develop a thermal extraction (TE) method for the determination of the 16 U.S. Environmental Protection Agency specified priority PAH pollutants in fly ash. The commonly used method for determining PAHs in solid wastes is solvent extraction followed by gas chromatography (GC) or GC–mass spectrometry (MS) analysis. This method is work- and time-intensive and produces solvent waste. In this study, the samples are analyzed using TE and fast GC–time-of-flight (TOF)-MS. The complete process from extraction to analysis can be achieved in less than one hour. The results indicate that the TE–GC–TOF-MS method has good linear range from 1.5 to 60 µg/g for all 16 PAHs. The recoveries for the 16 target PAHs vary between 83% and 94%.

Introduction

Natural solid wastes have been an environmental concern over the years because they may contain harmful or toxic chemicals. Many of these chemicals can contaminate the environment and harm humans when they are released without treatment. In order to better deal with solid waste problems, investigation of the nature and behavior of polycyclic aromatic hydrocarbons (PAHs) is important. PAHs are a class of semivolatile organic compounds sometimes produced in combustion systems (1). There are a number of epidemiologic and mortality studies that show increased incidences of cancer in humans exposed to mixtures of PAHs (2). Mortality studies have demonstrated that exposure to environments that contain a variety of PAHs caused increased incidences of lung and genitourinary cancer mortality, in addition to skin tumors (3,4). All 15 PAHs specified in the Ninth Report on Carcinogens (5) may form as a result of incomplete combustion of organic materials. Over 100 PAHs exist in gaseous, liquid, or solid matrices in the environment. The U.S. Environmental Protection Agency (EPA) has specified 16 PAHs on its priority pollutants list (6).

Fly ash is a postcombustion particulate residue. It contains various inorganic and organic compounds, some of which have been identified as environmental pollutants such as mercury and PAHs. There is no doubt that both qualitative and quantitative data about these materials are important in relation to fly ash disposal.

Most current methods of analysis for semivolatile organic compounds, such as PAHs in solid samples, involve the extraction of the target compounds from the sample matrix with organic solvents, usually methylene chloride or a mixture of methylene chloride and other solvents. Analysis of the extracted compounds is normally accomplished using gas chromatography (GC) or GC coupled with mass spectrometry (MS) (7,8). The primary advantages of these analytical methods are high selectivity and sensitivity. The GC approach to molecular information is often hampered by a lack of volatility and is generally limited to aromatic systems of five or six condensed rings with molecular weights up to approximately 300 (9). To improve this situation, liquid chromatography (LC) has been investigated in conjunction with MS for the analysis of PAHs (10,11).

Besides the Soxhlet extraction technique, alternative techniques are the applications of supercritical fluid extraction, accelerated solvent extraction, and ultrasonic extraction (12,13). In general, the solvent extraction method generates secondary solvent waste that creates a disposal problem. Furthermore, the solvent extraction procedure and any additional cleanup and concentration steps are very labor-intensive and time-consuming in the laboratory. Typically, the Soxhlet extraction process may take from 6 to 24 h to perform and uses a variety of environmentally hazardous solvents (14).

In recent years, a solventless method for extracting semivolatile organic compounds has become a technique of interest (13). The U.S. EPA has published a standard method (Method 8275) to determine semivolatile organic compounds [PAHs and polychlo-

rinated biphenyls (PCBs)] in soils, sludges, and solid wastes by using thermal extraction (TE) coupled with the capillary GC–MS method (16). TE is a low-temperature method in which the final temperature is 340°C. At this temperature, carbon–carbon bonds remain unaltered by heating. The analytes are extracted from the solid samples by heating in a stream of inert gas (usually helium) to a temperature that is high enough to desorb the semivolatile organic compounds but low enough to avoid degrading the sample matrix itself. The evolved gases are swept through a heated transfer line and trapped for further separation and analysis. The overall analysis time required is generally 1 h. However, in order to use this EPA standard method, details of procedures of how to deal with combustion residues (fly ash and bed ash) still need to be developed.

The extracts are usually a mixture of PAHs. The determination of PAHs requires a method that can identify the compounds and quantitate them. In terms of chromatography, GC–MS (17) and LC–MS (11) are appropriate technologies to accomplish this purpose. In particular, computerized GC–MS has become a standard instrumental technique for determining organic chemicals in environmental samples over the last 20 years (19). GC–MS works very well for target compounds (i.e., those for which the instrument has been calibrated) and those that can be identified by looking for a specific mass spectrum at a specific retention time (20). Although the basic principles were worked out in the 1960's, fast- or high-speed GC has not created significant interest until recent years (21). The increasing application of time-of-flight (TOF)-MS has provided a catalyst for the application of fast GC. TOF-MS is ideal for fast GC because it is much faster than other mass analyzers. Compared with conventional GC–MS, fast GC–TOF-MS greatly reduces analysis time and even adds resolving power. It has been successfully applied in analyzing PCBs and a host of suspected endocrine disrupters.

The goal of this project is to determine 16 U.S. EPA priority pollutants in fly ashes from a fluidized bed combustion (FBC) system using TE and fast GC–TOF-MS. The analysis can be achieved in less than 1 h.

Experimental

Description of the method

The fly ash samples were collected during experiments with Western Kentucky University's bench scale FBC system. The samples were ground and mixed for 3 min in a shatter box in order to pass a 100-mesh (150-µm) sieve. The ground sample was then split into several portions using a Brinkman microsplitter (Brinkman Instruments, Westbury, NY), and stored in a refrigerator for further study.

TE followed by GC–TOF-MS

A sample of approximately 100 mg of fly ash was loaded into a quartz crucible, which was then placed into the ThermEx pyrocell (LECO Corporation, St. Hoseph, MI) and heated. The evolved gases formed from heating were then swept by helium to the cryogenic focusing system (CFS) cryocell. In the cryocell, the gases were trapped using liquid nitrogen, desorbed onto the GC capillary column, and then analyzed by the GC–TOF-MS. The LECO Pegasus II GC–TOF-MS was equipped with a 60,000 compound National Institute of Standards and Technology (NIST) data base, which was used for the analysis of the samples. Helium was the carrier gas. The capillary column used was a 30-m × 0.32-mm × 0.25-µm Hewlett-Packard-5 (Palo Alto, CA). The temperature of the transfer line was 300°C. The mass spectrometer was operated in the selected ion mode for each of the 16 PAHs specified by the EPA. The temperature programming parameters for the ThermEx Inlet system are listed in Table I. Quantitative analysis was carried out using calibration curves of the PAH standard, which contained the 16 PAHs specified by the EPA.

Table I. The Heating Programs Used for Optimization of the Thermal Extraction Conditions

Heating condition	Step	Initial temp. (°C)	Rate (°C/min)	Final temp. (°C)	Isothermal temp. (min)	Total time (min)
1	1	45	–	45	0.5	
	2	45	10	340	10.0	
	3	340	100	45	0	43.0
2	1	45	–	45	0.5	
	2	45	10	200	25.0	
	3	200	100	45	0.0	
	4	45	100	200	0.0	
	5	200	10	340	24.5	
	6	340	100	45	0.0	85.5
3	1	45	–	45	0.5	
	2	45	10	200	70.0	
	3	200	100	45	0.0	
	4	45	100	200	0.0	
	5	200	10	340	24.5	
	6	340	100	45	0.0	144.5
4	1	60	–	60	0.5	
	2	60	35	280	30.0	
	3	280	35	340	3.0	
	4	340	100	280	1.0	
	5	280	100	60	–	45.3

Solvent extraction method

The fly ashes were extracted using a Tecator Soxtec 1045 extraction system (Fisher Scientific, Pittsburgh, PA). The extractor was first heated to 110°C for a period of 1 h to clean the apparatus. Once cleaned, 6–15 g of the ash were placed in the extraction thimble, the thimble and the ash were placed inside the apparatus, and the extract was heated with refluxing methylene chloride (80 mL) for 5 h. The extract was then concentrated to 1 mL using a Kuderna–Danish concentrator before GC–MS analysis.

Once the extraction and concentration was completed, a Shimadzu QP 5000 system with an NIST–EPA 62,000-compound database was used for GC–MS analysis. Two-microliter aliquots of the samples were injected, using the splitless mode, into the RTX-5 fused-silica capillary

column (60 m × 0.32 mm) and a stationary phase thickness (5% phenylmethyl polysiloxane) of 1 µm. Helium was the carrier gas. The GC oven conditions used for PAH analysis were as follow: held at the initial temperature of 70°C for 1 min, heated to 150°C at 8°C/min, heat to 250°C at 5°C/min and held 5 min, and heated to 300°C at 7°C/min and held for 5 min. The temperature for the interface, injector, and detector was 230°C. The mass spectrometer was operated in two modes: the scan mode and the selected ion monitoring (SIM) mode. The scan mode was used for determining the PAH retention times and the SIM mode was used for the analysis of the PAHs. Quantitation of the PAHs was performed using calibration curves constructed from the GC–MS analysis of PAHs in methylene chloride solutions prepared from a standard PAH solution, 2000 µg/mL each in methylene chloride.

Materials

Ash samples

All test samples were collected from a 0.1 MW_{th} (megawatts, thermal input) bench scale FBC system. Fly ash samples were collected using a high-efficiency sampling cyclone operating at a high temperature (~ 400°C) at a location before the gas exhaust pipe. The collection was started 8 h after the combustion conditions were changed and stabilized. The sampling time was 2 h.

Reagents

The standard PAH mixture solution, 2000 µg/mL each in methylene chloride–benzene (50:50), naphthalene-d_8 (internal standard, 2000 µg/mL in methylene chloride), anthracene-d_{10} (internal standard, 2000 µg/mL in methylene chloride), and benzo[a]anthracene-d_{12} (internal standard, 2000 µg/mL in methylene chloride) were all purchased from Supelco (Bellefonte, PA). Methanol (purge-and-trap grade, cat. no. 48093) and methylene chloride (capillary GC grade) were purchased from Aldrich Chemical Company (St. Louis, MO).

Apparatus

A LECO Pegasus II GC–TOF-MS and ThermEx Inlet system were used in this study. Once the sample was loaded, the system was automatically controlled with the computer. The ThermEx Inlet System (LECO) was designed to heat small quantities of solid or nonvolatile liquid samples in a porous quartz pyrocell and transfer the evolved sample components to a heated capillary GC injection port. In this system, helium as the sweeping gas provided an inert surrounding such that the sample and any volatilized compounds were permitted to contact only heated fused quartz surfaces during the extraction and transfer to the GC injection port. All zones in the sample transfer path can be kept at 300°C or greater. The unit also has a bakeout capability of 700°C in the TE chamber and 450°C in the interface zone. A LECO Model 9730 CFS independent liquid–nitrogen trapping system was used for cryofocusing compounds at the head of a capillary column. The low mass heater design allows desorption heating rates of greater than 1700°C/min so that even very volatile compounds can elute as sharply focused peaks. A high-speed GC system (HP 6890 Plus, Agilent Technologies, Palo Alto, CA) was linked to the TOF-MS. The oven temperature of the GC (with HP-5 capillary column, 30 m × 0.32 nm × 0.25 µm) can be controlled from ambient to 450°C, and has programmable oven heating controls capable of rates up to 120°C/min and fast cool-down to minimize cycle time. The GC oven conditions used for these experiments were as follows held at the initial temperature of 35°C for 44.3 min, ramped to 315°C at 35°C/min, then held at 315°C for 2 min. The TOF-MS used reflecting ion optics to double the length of the drift tube, which improved the mass resolution at the detector. The system has an acquisition rate of up to 500 full-range (5–1000 amu) mass spectra per second, using a nominal electron energy of 70 eV in the electron impact ionization mode.

Standards preparation

PAH-free ash blank preparation.

An ash blank used for the preparation of the calibration standard ash was prepared as follows: ash collected from the FBC facility was ground in a mortar and pestle so as to pass through a 100-mesh (150-µm) sieve, the sieved ash was heated to 950°C in an air atmosphere in a muffle furnace for 8 h, the heated ash was then tested using TE and GC–TOF-MS analysis to ensure that no organic compounds were left in the ash, and the heating and analysis steps were repeated until no organic compounds could be detected.

PAH-containing ash standards preparation

To prepare ash standards with different amounts of PAHs, portions of the PAH-free ash blank (~ 1 g) were weighed into 2-mL amber vials. The ash was then spiked with the standard PAH mixture (2000 µg/mL), which was also weighed into the vials. The internal standards (naphthalene-d_8, anthracene-d_{10}, and benzo[a]anthracence-d_{12}) were also added. Methanol and methylene chloride were added to the sample vials to assist in distributing the standard compounds homogeneously throughout the ash. The vials were sealed and shaken frequently. The samples were left at room temperature for more than five days to allow the PAHs to mix thoroughly. Then the vials were opened in order to completely evaporate the solvent. Each standard sample was stored at –10°C to –20°C and protected from exposure to light and moisture. Typical PAH-spiked standard ash samples had concentrations of 20–60 µg/g.

Results and Discussion

Preliminary test of PAHs in fly ash

A sample of fly ash was analyzed according to the recommended conditions in EPA Method 8275—*Semivolatile Organic Compounds (PAHs and PCBs) in Soil/Sludges and Solid Wastes Using Thermal Extraction/Gas Chromatography/Mass Spectrometry*. The TE profile was set as follows: hold at 60°C for 2 min, raise from 60°C to 340°C in 8 min, hold at 340°C for 3 min, and cool from 340°C to 60°C in 4 min. The NIST electronic library identified four possible PAHs with molecular weights of 128 (naphthalene), 152 (acenaphthylene), and 178 (phenanthrene and anthracene) from the GC–TOF-MS chromatogram of the sample. However, reheating the sample produced compounds with peaks at *m/z* 128 and 178, yet another 10-min isothermal heating at 340°C produced peaks corresponding to *m/z* 128 and 202. These results indicated that the TE conditions had to be modified so that the PAHs in the fly ash sample could be effectively extracted.

Optimization of the TE conditions

In order to investigate the effect of temperature, heating rate, and the heating process for PAHs being released from ash samples, several different heating programs were investigated with the ThermEx Inlet system. The purpose of the tests was to determine optimized experimental conditions for TE. A typical set of trial runs is shown in Table I. A longer isothermal step was used at the high final temperature in the first condition. An intermediate temperature (200°C) between the initial and final temperature was chosen for test conditions 2 and 3 to allow an isothermal period for more complete extraction of the lower molecular weight materials. In the second condition, the isothermal time at the high final temperature was approximately 15 min longer than that in the first condition. The third condition had a longer holding time at the intermediate temperature (200°C) than that in the second condition. In the fourth condition, a higher intermediate temperature (280°C) was chosen because it is close to the vaporization temperatures of acenaphthylene and acenaphthene and higher than that of naphthalene. There were no significant peaks identified as PAHs when an additional heating of 15 min was applied to each condition after the analysis process was over.

As a way of comparing results from the optimization tests, the peak area-to-sample weight ratios for some selected PAHs were calculated and are listed in Table II. The results listed in the table show that all conditions could be used for PAH analysis in the ash samples because the peak area-to-sample weight ratios for all PAHs calculated from each condition were relatively close. The discrepancies between each set of conditions is in the range of ± 10%. Most small molecules are released at lower temperatures; for instance, naphthalene makes up 74.6% of the total PAH determined in the ash sample at 200°C, as indicated in the second condition. The larger molecules are released at higher temperatures. As shown in Table II, smaller amounts of some of the larger molecules (acenapthylene, anthracene, and pyrene) were detected during the lower temperature heating processes used in the second and third conditions. In this study, the fourth condition was preferred because it showed generally higher peak area-to-sample weight ratios and required a shorter time.

Table II. Analysis Results from the Study of Different Heating Conditions on Peak Area-to-Sample Weight Ratios*

	Compounds				
Conditions	Napthalene	Acenapthylene	Anthracene	Fluoranthene	Pyrene
1 45–340°C	90579	5821	14220	35711	28917
2 45–200°C 200–340°C	90855	5607	16570	37772	27873
3 45–200°C 200–340°C	89699	5616	15870	36175	27105
4 60–340°C	92103	6089	17370	34810	30012
Avg.	90787	5783	16008	36117	28477
M.D.	1.35	5.29	8.51	4.58	5.39

* Counts/mg.
† Avg., average and M.D., maximum deviation (%).

Based on the above results, the TE profiles were set as follow: the ThermEx transfer line (1 m) temperature was 310°C; the ThermEx interface oven temperature was 320°C; the ThermEx sweep gas pressure was He at 10 psi; and the ThermEx heating profile was described in the fourth condition. Finally, the CFS parameters were the following: because CFS has trap and desorption functions, its profile should match the steps of both the ThermEx and GC–TOFMS systems. Its operating conditions were set at –50°C to 315°C in 1.5 min, isothermal at 315°C for 6.5 min, then from 315°C to –50°C in 1.5 min.

Table III. Mean Recovery and RSDs Obtained from TE–GC–TOF-MS Analysis

Peak no.	Compound	Content determined in sample (µg/g)			Mean recovery (%)	RSD (%)
1	Naphthalene	48.3	49.4	53.3	94	2.7
2	Acenaphthylene	45.0	48.8	53.4	92	1.3
3	Acenaphthene	48.3	51.8	54.2	96	1.4
4	Fluorene	41.8	43.5	49.8	84	2.7
5	Phenanthrene	44.7	47.5	51.1	89	0.7
6	Anthracene	41.3	44.3	48.8	84	1.2
7	Fluoranthene	41.8	43.0	48.5	83	2.3
8	Pyrene	42.8	44.7	48.8	85	0.8
9	Benz[a]anthracene	42.1	43.9	47.7	83	1.3
10	Chrysene	42.8	44.9	49.0	85	1.1
11	Benz[b]fluoranthene	44.2	44.9	50.5	87	2.7
12	Benz[k]fluoranthene	43.1	45.3	49.5	86	1.1
13	Benz[a]pyrene	42.0	43.3	48.1	83	1.9
14	Indeno[1,2,3-cd]pyrene	42.5	44.1	46.6	83	2.2
15	Dibenzo[a,h]anthracene	43.1	44.9	48.2	84	1.7
16	Benz[ghi]perylene	42.2	43.0	49.0	84	2.8
	Original amount of each	49.7	53.5	57.4		

TE–GC–TOF-MS analysis of ash standard

Prepared ash standards were analyzed using the optimized TE–GC–TOF-MS method. During the ThermEx heating period, the GC oven remained at the initial temperature, and no data were collected by the MS system. When the CFS started desorption, the GC ran its temperature program and the TOF-MS started data acquisition. The actual GC running time was only 10 min. All 16 priority pollutant PAHs were clearly separated, as shown on the chromatogram in Figure 1. All 16 target PAHs and 3 internal standards in the sample were identified through the NIST electronic library. The order of the isomers was determined according to U.S. EPA Method 8275.

A comparison of GC retention times between the conventional GC–MS (Shimadzu QP 5000 system) and rapid GC–TOF-MS (LECO Pegasus II) for the 16 PAHs showed that the GC–TOF-MS system would complete the entire analysis in less than 11 min, and the conventional GC–MS system required 56 min for completion. The GC–TOF-MS system gave baseline resolution of the 16 priority

PAHs, but the conventional GC–MS did not. The entire TE and analysis process using TE–GC–TOF-MS required only 45 min to complete.

Five standard fly ash samples, which contained different concentrations of PAHs, were analyzed using the optimized TE–GC–TOF-MS system. The peak area (computed by the instrument program based on the parameters, start of peak, end of peak, valley point, and any tangent points) was calculated and compared with the weight of each PAH in the standard fly ash sample. The linear working range for quantitation was determined [square of the coefficient of correlation (R) for the calibration curve was 0.99 or above] to be 1.5–60 mg/g for all 16 PAHs. These calibration data were stored for further quantitation calculations.

Mean recovery of the TE–GC–TOF-MS technique

Three different standard ash samples with different PAH amounts were tested on three different days to determine the recovery of the TE–GC–TOF-MS technique for analyzing ashes.

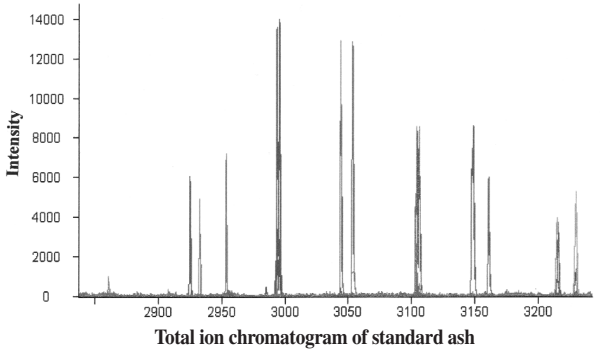

Figure 1. Total ion chromatogram of standard ash. Left to right: Naphthalene-d8 (IS), naphthalene, acenaphthylene, acenaphthene, fluorene, anthracene-d_{10} (IS), phenanthrene, anthracene, fluoranthene, pyrene, benz[a]-anthracene-d_{12} (IS), benz[a]anthracene, chrysene, benzo[b]fluoranthene, benzo[k]fluoranthene, benzo[a]pyrene, indeno[1,2,3-cd]pyrene, dibenz-[a,h]anthracene, and benzo[ghi]perylene.

Table IV. LODs Obtained from the TE–TC–TOF-MS Analysis

Peak no.	Compound	LOD (µg/g)
1	Naphthalene	1.43
2	Acenaphthylene	1.24
3	Acenaphthene	1.39
4.	Fluorene	1.13
5	Phenanthrene	1.36
6	Anthracene	0.53
7	Fluoranthene	0.35
8	Pyrene	0.89
9	Benz[a]anthracene	0.77
10	Chrysene	1.31
11	Benz[b]fluoranthene	0.71
12	Benz[k]fluoranthene	0.92
13	Benz[a]pyrene	0.89
14	Indeno[1,2,3-cd]pyrene	0.92
15	Dibenzo[a,h]anthracene	0.69
16	Benz[ghi]perylene	1.11

The original concentrations, the measured concentrations, the mean recoveries, and the relative standard deviations (RSDs) are shown in Table III. The data listed in the table shows that the recoveries varied from 83% to 96% for different PAHs. Generally, PAHs with higher molecular weights had relatively lower recoveries because of their higher boiling points. Another reason might be larger PAHs are adsorbed more tightly by the ash particles. By comparison, the solvent extraction method gave lower recoveries for lower-molecular-weight PAHs and higher recoveries for higher molecular weight PAHs. When the fly ash sample with the same source was extracted by Soxhlet extraction, the recoveries for the three surrogates were 83% for naphthalene-d_8, 88% for anthracene-d_{10}, and 90% for benz[a]anthracene-d_{12}, respectively. The PAHs with low molecular weights may be lost during solvent extraction because they are more volatile and harder to keep in the solution during the refluxing/extraction and concentration processes. However, in TE, the evolved gases were trapped directly at the head of the GC column without refluxing and concentration procedures, thus avoiding loss of evolved PAHs.

Limit of detection for TE–GC–TOF-MS method

Seven blank fly ash samples (~ 70 mg each) were analyzed using the optimized TE–GC–TOF-MS method on different days.

Table V. Analysis Results for PAHs in Fly Ash Sample A

Compound	Thermal extraction (µg/g)	Solvent extraction (µg/g)
Naphthalene	138.3	109.2
Acenaphthylene	53.3	58.1
Acenaphthene	28.4	18.3
Fluorene	15.6	16.6
Phenanthrene	50.3	46.3
Anthracene	36.9	21.1
Fluoranthene	33.8	22.2
Pyrene	39.4	35.0
Total	**395.0**	**326.8**

Table VI. Analysis Results for PAHs in the Fly Ash Sample B

Compound	TE (µg/g)	Soxhlet extraction (µg/g)
Naphthalene	149.8	70.9
Acenaphthylene	49.5	60.3
Acenaphthene	50.3	24.5
Fluorene	22.7	19.7
Phenanthrene	27.0	43.2
Anthracene	21.0	25.0
Fluoranthene	16.7	29.8
Pyrene	27.3	53.2
Benz[a]anthracene	2.5	ND*
Chrysene	8.9	8.8
Benzo[b]fluoranthene	44.2	47.5
Benzo[k]fluoranthene	3.9	ND
Total	**423.8**	**382.9**

* Not detected.

The limit of detection (LOD = 3 × standard deviation of the blank signal) was calculated from the baseline noise signals at the expected retention time for individual target PAHs. The LOD for each PAH is shown in Table IV.

Analysis of fly ash samples from the FBC system

Dozens of fly ash samples collected from the FBC system were analyzed using the optimized TE–GC–TOF-MS method. Two of them (referred to as Ash A and Ash B) were selected for comparison analysis between TE and solvent extraction. Tables V and VI are the quantitation results from TE for samples A and B, respectively. The quantitation data were calculated from the relationships between concentration and compound peak areas, that were obtained from the instrument calibration step. By way of comparison, the results from the solvent extraction with the Soxhlet extractor for the two samples were also included in the two tables. All the concentrations were the average values of two runs and were already adjusted to the concentration level in the original fly ashes. For sample A, the amounts used in TE were 19.8 and 29.5 mg, and the amounts used in the Soxhlet extraction were 6.0 and 6.9 g. As for sample B, 6.8 and 11.6 mg were used for two TE runs and 2.8 g and 3.0 g were taken for the duplicate solvent extractions, respectively.

The results indicate that the TE method was comparable (in terms of the magnitude of the total PAHs) with the traditional Soxhlet extraction method for the total amount of PAHs in a single sample. However, the concentrations of individual PAHs may vary in the two methods because these compounds may have had differing behavior in the TE and in the Soxhlet extraction process, especially naphthalene, which showed significant differences. This difference may be attributed to the higher volatility of naphthalene.

Conclusion

Based on the data presented in this study, the following observations and conclusions can be made. TE combined with GC–TOF-MS shows good linearity and recoveries for determining PAHs in ash. It is a time-saving and solvent-free method. In addition, less sample is required in this method. The TE–GC–TOF-MS procedure is comparable with, and is more effective than, the conventional solvent extraction combined with GC–MS for PAH analysis. It can be applied to determine other semivolatile organic compounds in solid wastes as long as the experimental conditions are adjusted accordingly.

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References

1. W. Bartok and A.F. Sarofim. *Fossil Fuel Combustion: A Source Book*. John Wiley, New York, NY, 1991, p. 269.
2. Agency for Toxic Substances and Disease Registry (ATSDR). *Toxicological Profile for Polycyclic Aromatic Hydrocarbons (PAHs), Update, (Final Report, August 1995).* ATSDR, Public Health Service, U.S. Department of Health and Human Services, Atlanta, GA, 1995, p. 482, NTIS Accession No. PB95-264370.
3. International Agency for Research on Cancer (IARC). *IARC Monographs on the Evaluation of the Carcinogenic Risk of Chemical to Humans, Polynuclear Aromatic Compounds, Part 3. Industrial Exposures in Aluminum Production, Coal Gasification, Coke Production and Iron and Steel Founding,* vol. 34. IARC, Lyon, France, 1984, p. 219.
4. T.R. Barfknecht. Toxicology of soot. *Energy Combust. Sci.* **9:** 199–237 (1983).
5. National Toxicology Program. *Ninth Report on Carcinogens (Revised January 2001).* Public Health Service, U.S. Department of Health and Human Services, http://ehis.niehs.nih.gov/roc/toc9.html (accessed January 2001).
6. U.S. EPA. *List of the Sixteen PAHs with Highest Carcinogenic Effect.* IEA Coal Research, London, U.K., 1984.
7. A.M. Mastral, M. Callen, C. Mayoral, and J. Galban. Polycyclic aromatic hydrocarbon emissions from fluidized bed combustion of coal. *Fuel* **74:** 1762–66 (1995).
8. L. Wheatley, Y.A. Levendis, and P. Vouros. Exploratory study of the combustion and PAH emissions of selected municipal waste plastics. *Environ. Sci. Technol.* **27:** 2885 (1993).
9. P. Burchill, A.A. Herod, and R.G. James. *Carcinogenesis,* vol. 3. *Polynuclear Aromatic Hydrocarbons,* Raven Press, New York, NY, 1978, p. 35.
10. W.A. Dark, W.H. McFadden, and D.L. Bradford. Fractionation of coal liquids by HPLC with structural characterization by LC–MS. *J. Chromatogr. Sci.* **15:** 454–460 (1977).
11. W.A. Dark and W.H. McFadden. The role of HPLC and LC–MS in the separation and characterization of coal liquefaction products. *J. Chromatogr. Sci.* **16:** 289–93 (1978).
12. V. Janda, K. Bartle, and A. Clifford. Review: supercritical fluid extraction in environmental analysis. *J. Chromatogr.* **642:** 283–99 (1993).
13. S. Purushothama, W.-P. Pan, J.T. Riley, and W.G. Lloyd. Analysis of polynuclear aromatic hydrocarbons from coal fly ash. *Fuel Process. Technol.* **53:** 235–42 (1998).
14. F. Lee and D. Schueltzle. In *Handbook of Polycyclic Aromatic Hydrocarbons,* vol. 1. A. Bjorseth, Ed. M. Dekker, New York, NY, 1985.
15. D. King and B. Belair. *Analysis of PCBs in Soils and Sludges Using Thermal Extraction-GC-MS.* Hewlett Packard Company, Wilmington, DE, June 1993. Application Note 228–29.
16. U.S. EPA. *Method 8275: Semivolatile Organic Compounds (PAHs and PCBs) in Soil/Sludges and Solid Wastes Using Thermal Extraction/Gas Chromatography/Mass Spectrometery (TE/GC/MS).* EPA, Research Triangle Park, NC, December 1996.
17. U.S. EPA. *Method 8270D: Semivolatile Organic Compounds by Gas Chromatography/Mass Spectrometry.* EPA, Research Triangle Park, NC, January 1998.
18. R.E. Finnigan, D.W. Hoyt, and D.E. Smith. Priority pollutants II-cost effective analysis. *Envir. Sci. Tech.* **13:** 534–41 (1979).
19. W.P. Eckel. "Making sense of nontarget compound data from GC-MS library searches". *American Laboratory.* **32(6):** 17–20 (2000).
20. R. Stevenson. "New instruments for separation science at PITTCON 2000: The new age of alliances?" *American Laboratory.* **32(10):** 19–42 (2000).

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