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Feasibility of Analyzing Fine Particulate Matter in Air Using Solid-Phase Extraction Membranes and Dynamic Subcritical Water Extraction

Johanna Tollbäck,[†] María Blasco Bigatá,^{†,*} Carlo Crescenzi,^{*,†} and Johan Ström[§]

Departments of Analytical Chemistry and Applied Environmental Science (ITM), Stockholm University, Stockholm, S-106 91, Sweden

We have evaluated the feasibility of using Empore solid-phase extraction (SPE) membranes as an alternative to conventional techniques for sampling fine airborne particulate matter (PM), including nanoparticles, utilizing a scanning mobility particle sizer (SMPS) and a condensation particle counter to evaluate their efficiency for trapping fine particles in the 10–800 nm size range. The results demonstrate that the membranes can efficiently trap these particles and can then be conveniently packed into an extraction cell and extracted under matrix solid-phase dispersion (MSPD) conditions. The potential utility of sampling PM using Empore membranes followed by dynamic subcritical water extraction (DSWE) for fast, efficient, class-selective extraction of polycyclic aromatic hydrocarbons (PAHs) associated with the particles, prior to changing the solvent and analysis by GC/MS, was then explored. The performance of the method was tested using National Institute of Standards and Technology (NIST)-certified “urban dust” reference material (SRM 1649a) and real samples collected at a site in central Rome with heavy road traffic. The method appears to provide comparable extraction efficiency to that of conventional techniques and with using GC/MS, detection limits ranged in the few picograms per cubic meter level. Sampling PM by Empore membranes may reduce the risks of losses of semivolatile compounds, while allowing relatively high sampling flow rates and safe sample storage. Moreover, the combination of MSPD with DSWE permits specific fractions of the PM components to be eluted, thereby generating clean extracts and reducing both analysis time and sample manipulation.

Airborne particulate matter (PM) has well documented adverse health effects, and strong correlations between particulate concentrations and respiratory or cardiovascular problems have been

found in various epidemiological studies.^{1–3} Although most of the mass of aerosols is distributed in larger particles, the greatest concern has shifted from PM₁₀ (particles with diameters <10 μm) toward finer fractions, such as PM_{2.5}, and recently to ultrafine fractions, also called Aitken particles (diameter <0.1 μm).⁴ Despite intense research efforts and concern, further investigations are required to fully elucidate the processes involved in the formation, in the physicochemical parameters of these aerosols, and the health risks they pose.^{5–7}

Scanning mobility particle sizers (SMPSs) have proved to be valuable tools for evaluating particle size distributions in various atmospheric environments.⁸ Aerosol particles are introduced into a DMA (differential mobility analyzer) with a typical geometric setup of two concentric cylinders. The aerosol particles are classified according to their electrical mobility by varying the electrical field between the cylinders. The particles in the sample air from the DMA are counted using a CPC (condensation particle counter) whereby the very small particles are grown by condensation of vapors to a laser detectable size.

In addition to size, chemical characterization is essential for elucidating toxicity mechanisms, for identifying sources of airborne particulate matter (source apportionment) and, thus, for implementing environmental policies designed to reduce emissions from major sources of particulates. The chemical composition of PM can be investigated online with particle sizers using aerosol mass spectrometry (AMS)^{9–12} or two-step laser mass

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* To whom correspondences should be addressed. E-mail: carlo.crescenzi@anchem.su.se. Phone: +46 8 162428. Fax: +46 8 156391. Department of Analytical Chemistry, Stockholm University, Arrhenius Laboratory of Natural Sciences, S-106 91, Sweden.

[†] Department of Analytical Chemistry, Stockholm University.

[‡] Current address: Departamento de Química Analítica, Centro Politécnico Superior, Universidad de Zaragoza, María de Luna 3, 50018, Zaragoza, Spain.

[§] Department of Applied Environmental Science (ITM), Stockholm University.

spectrometry (L2MS).¹³ However, a major advantage of off-line techniques is the scope they afford for investigating the averaged composition of much larger numbers of particles and fractionating different classes of chemical compounds.

Relatively straightforward methods requiring little or no sample preparation for analyzing the inorganic fractions of particles (elemental and/or metal analysis) are well established, but analysis of organic compounds has usually involved more complex and time-consuming extraction and analytical techniques, e.g., Soxhlet extraction followed by GC/HPLC–MS analysis.¹⁴

Polycyclic aromatic hydrocarbons (PAHs) are generally considered among the most abundant hazardous organic contaminants associated with airborne particulate matter.^{15–18} Because of their reactivity and volatility, losses of PAHs during sampling are almost unavoidable, adding significant errors to analyses of sampled airborne PAHs.¹⁹

Glass fiber filters are often used for sampling PAHs since they allow high flow rates to be applied. Other sampling media that have been tested include polyurethane foam,^{20,21} polymers,^{22–24} and cyclodextrins.²⁵ The potential utility and advantages of conventional solid-phase extraction (SPE) cartridges for air sampling have also been previously discussed.²⁶ Another possibility is to use Empore SPE membranes, consisting of polytetrafluoroethylene (PTFE) fibrils impregnated with small particles of a solid sorbent that provide a trapped stationary phase on which airborne analytes can be absorbed. Such membranes have high sampling capacity and might stabilize the analytes during storage of the samples.²⁷ SPE membranes have been mostly used for water sampling, but they have also been used to extract warfare agents,²⁸ nitroaromatic compounds,²⁹ and phosphate esters from the air.³⁰

SPE membranes have several advantages over SPE cartridges.³¹ First, their format allows relatively higher sampling flow rates. A further major reported advantage is that they have higher chromatographic efficiency due to the smaller particle size of the sorbent (10 μm instead of 40–80 μm). Membranes also have lower void volumes, higher surface areas per unit bed volume, and the uniformity of packing reduces breakthrough and channeling problems.

In conventional extraction methods, an organic solvent is used as the extracting phase and thus normally involves several laborious, time-, and solvent-consuming steps. Techniques such as Soxhlet extraction¹⁸ and sonication¹⁷ have also been widely used for extracting PAHs, and other associated organic compounds, from particulate matter. However, new extraction techniques have been proposed recently in order to reduce the time, sample handling, and solvent requirements, such as supercritical fluid extraction (SFE), accelerated solvent extraction (ASE), microwave-assisted extraction (MAE), dynamic sonication-assisted solvent extraction (DSASE), and subcritical water extraction (SWE).

When an extraction method is developed, only relative recoveries of the targeted analytes and the amount of organic solvent required are usually discussed. However, other chemical aspects of the extraction method are also important, notably its selectivity for the target analytes in complex matrixes relative to other compounds that may interfere with, and cause errors in, the analytical steps. A further recent tendency in the development of analytical methods is to use “green chemistry” approaches where possible, avoiding the use of organic solvents, or at least reducing the amounts used, because of their hazardous nature and disposal costs.³²

The extraction technique investigated in this work, subcritical water extraction (SWE), also called “hot water extraction”, “pressurized (hot) water extraction”, “superheated water extraction”, fulfills all the abovementioned criteria, including the potential for extracting selected fractions. As first reported in 1994 by Hawthorne et al.,³³ an environmentally friendly solvent like water can be effective for extracting a wide variety of organic compounds from diverse matrixes but not for many other organic compounds that have extremely low solubility in water due to its polarity. However when its temperature is increased sufficiently, water’s polarity is dramatically reduced and, hence, the solubility of the latter type of organic compounds in water is enhanced.^{34,35} Besides changing its polarity, higher temperatures also sharply decrease the viscosity and surface tension of water, thereby improving its ability to penetrate matrix particles as well as increasing the solubility of organic compounds in it.³⁶ Unlike temperature, pressure per se has weak effects on water’s polarity and just 2.0 MPa are required to maintain water in the liquid state at temperatures higher than 250 °C. Taking advantage of these

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properties, in recent years, SWE has been widely applied for selective extraction by applying appropriate temperatures and pressures.³⁷ This method has been used for extracting organic pollutants from a variety of matrixes, such as urban dust, soils, sediments, and foodstuff, e.g., phenols, *n*-alkanes, and PAHs from soil. For instance, while polar analytes like phenols are quantitatively extracted at 100 °C and 5.0 MPa, nonpolar compounds such as PAHs and *n*-alkanes are still retained in the matrix. PAHs are effectively removed from the matrix when the temperature and pressure are increased to 250 °C and 5.0 MPa, respectively. However, the high molecular mass alkanes are only extracted if temperatures higher than 300 °C are applied or if the pressure is reduced to 0.5 MPa to generate steam.^{34,37} Successful extraction of PCBs from soil using SWE followed by solvent trapping and then a liquid–liquid extraction has also been reported by Yang et al. in 1995.³⁸ SWE has been coupled with solid-phase microextraction (SPME) for preconcentrating PAHs, PCBs, and natural pyrethrins before analysis.^{39–41} It has also been coupled online with Carbograp 4 solid-phase extraction cartridges for determining pesticides in soils.^{36,42,43,44} In addition, Hawthorne et al. developed a method for extracting PAHs from soils, sediments, and airborne particulate matter, in which analytes were collected on a styrene–divinylbenzene (SDB) SPE disk after static SWE.³⁵ The potential utility of coupling static SWE with SPE has also been evaluated for determining pesticides and PAHs in compost.⁴⁵

The aims of the study presented here were to investigate the feasibility of using Empore disk SPE membranes as alternative devices for sampling fine airborne particulate matter and to develop a procedure for their subsequent extraction using dynamic subcritical water extraction.

EXPERIMENTAL SECTION

Chemicals and Standards. A certified polycyclic aromatic hydrocarbons standard solution (PAH-9 mix, 10 ng/μL) containing naphthalene, acenaphthylene, acenaphthene, fluorene, anthracene, phenanthrene, chrysene, pyrene, benzo[*a*]pyrene, fluoranthene, benzo[*b*]fluoranthene, benzo[*k*]fluoranthene, benz[*a*]anthracene, indeno[1,2,3-*c,d*]pyrene, dibenz[*a,h*]anthracene, and benzo[*ghi*]perylene was supplied by Dr. Ehrenstofer GmbH (Germany). A standard spiking solution, containing C₈–C₃₃ *n*-alkanes at concentrations of 10 ng/mL, was prepared. For the GC-FID analysis, 2,2 binaftyl was added prior to the injection as a volumetric standard. For the GC/MS analysis, a mixture of deuterated PAHs (PAH-9, 10 ng/μL) was used as a volumetric standard and surrogate standard for the real samples.

In the preliminary GC-FID experiments (see below), standard solutions were prepared at concentrations of 1 ng/μL, and for the urban dust analysis by GC/MS, the standard concentrations were 12–60 pg/μL.

The C8, SDB-RPS and SDB-XC Empore disks were purchased from 3M Filtration Products (St. Paul, MN). All the membranes were 47 mm in diameter. HPLC-grade water was produced using a Milli-Q purification system (Millipore), and all solvents used were HPLC grade: hexane and acetone provided by Merck (Walkerburn, Germany).

Scanning Mobility Particle Sizer (SMPS). The SMPS was used to determine the aerosol size distribution of particles between 10 and 800 nm in diameter. The experimental setup included a constant output atomizer from Thermal Systems Incorporated (TSI, model 3076) to generate a polydisperse aerosol. The solution used to generate aerosol sprays was normal tap water, in which there were sufficient impurities (salts) to produce a large number of small particles.

The sample air was directed to a 3-way valve, from which one path led to the filter device and the other directly to a T-connection combining the two paths before the air was directed to the SMPS (TSI-3071A) coupled to a condensation particle counter (TSI-3022A). Apart from the filter device, the two sample paths were identical in terms of the material, diameter, and length of tube involved. Thus, by switching the valve we could make repeatable measurements of the size distribution of the aerosol before and after passage through the filter. The ratios of these measurements indicate the transfer efficiency of the particles as a function of size, assuming that their size does not change during passage through the filter. Results obtained with Empore SPE membranes were compared with data obtained from a total particle filter installed in front of the tested filter setup.

Sample Collection and Preparation. Prior to each experiment, the membranes were washed with 5 × 5 mL of acetone in a glass frit Büchner funnel and air-dried. The selective DSWE extraction method was carried out by spiking membranes as follows. A C8 Empore disk was placed in the holder previously described⁴⁶ between two Teflon rings, the holder was connected to the VDE 0530 KNF (Neuberger, Freiburg, Germany) pump, and the membrane was spiked with 100 μL of a standard solution containing a mixture of 16 PAHs in cyclohexane and 100 μL of a standard solution containing a mixture of C₈–C₃₃ *n*-alkanes, each at a concentration of 10 ng/μL, while air was pumped through the membrane. After the spiking, the membrane was put on a new filter paper sheet, folded twice, and cut using a lancet into 7–10 pieces, which were packed in the extraction cell (see below) and pressed into place with a wooden cylinder.

Optimal conditions were evaluated using membranes spiked by spreading SRM 1649a “urban dust” reference material at various levels over them. The membranes were then folded, cut, and packed as described above. Handling of the membranes with these conditions was easy. Particulate appears to stick on membrane surfaces, and once folded, losses are very implausible to occur. After the packing, the lancet and piston were rinsed with methanol.

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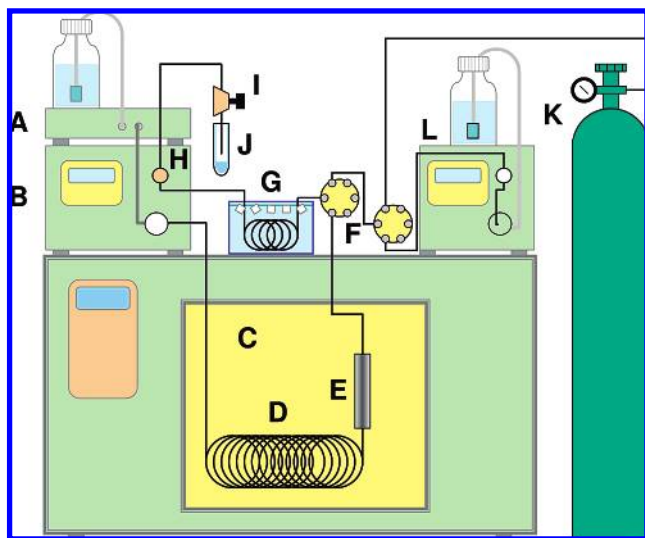


Figure 1. Sketch of the DSWE setup: (A) solvent (water) degasser; (B) HPLC pump module for pumping water; (C) GC oven; (D) stainless steel preheating coil; (E) extraction cell; (F) solvent selector; (G) ice–water bath; (H) pressure transducer of pump delivering water; (I) back-pressure regulator; (J) vial for extract collection; (K) purging gas (nitrogen); and (L) washing phase (hexane) pump.

Real airborne particulate matter samples were collected from a site in the central area of Rome (Italy) using the pump and holder previously described at a flow rate of 1.2 L/min. After, the sample membranes were stored in aluminum foil inside a clean polypropylene box.

Dynamic Subcritical Water Extraction Apparatus. A sketch of the dynamic SWE system is presented in Figure 1. The extraction system consisted of an LC-10AD pump (Shimadzu, Kyoto, Japan), which pumped HPLC-grade water through a 3.5 m stainless steel, preheating coil (internal diameter, i.d., 0.25 mm) connected to the extraction cell. Prior to use, oxygen in the water was displaced by nitrogen and the water was further degassed by an 1100 Agilent degassing system placed before the pump. The extraction cell consisted of an empty 4.6 mm i.d. \times 50 mm long stainless steel HPLC column supplied by Supelco (Bellefonte, PA). The temperature during the extraction was controlled using a 3400 Varian (Walnut Creek, CA) gas chromatographic oven. The cell was installed to ensure upward flow through the system, and after leaving the extraction cell, the extract was cooled by passage through a 30 cm, 0.25 mm i.d. stainless steel cooling coil placed in an ice–water bath. Solvent selector consists of two VICI, Valco Instruments Co. Inc (Houston, TX) six-port valves. An adjustable back pressure regulator (BPR) (Upchurch Scientific) was connected after the ice–water bath. To maintain water in its liquid state, the pressure was adjusted, at the required flow rate, with the BPR and controlled by the HPLC pump operating in constant pressure mode at 5.5 MPa. All connections between the different parts of the system before the trap were made of stainless steel 0.25 mm i.d. tubing.

Extraction Procedure. After the cell was packed, it was connected to the system (as previously described) and the water flow passing through the extraction cell was set to 2 mL/min and the pressure was adjusted to 5.5 MPa with the BPR and the HPLC pump operating in pressure-control mode. The cell was washed

with cold water for a few minutes to check for leaks and remove air from the system. The temperature was then increased to 80 °C, where it was held for 10 min. Afterward, the temperature was further increased to 130 °C and held for 10 min. After that, the washing temperature was set at 250 °C and the membrane was extracted with 35 mL of water (about 18 min). Water eluate was collected in glass vials containing 1 mL of hexane. After the extraction, the first valve of the solvent selector was switched and water was removed from the tubing using nitrogen. Finally, the second valve of the solvent selector was switched and tubing from the outlet of the cell was rinsed by pumping 1 mL of hexane through it with a 9002 Varian pump. PAHs were removed from the water extract by two consecutive liquid–liquid extractions with 2 mL of hexane. The final hexane extract was evaporated to a final volume of 500 μ L under a nitrogen stream. Samples spiked with standard solutions were analyzed by GC-FID, and all PM samples were analyzed by GC/MS.

GC-FID Analysis. In the preliminary study, the analytes were separated, identified, and quantified using a Hewlett-Packard HP 5890 series gas chromatograph equipped with a flame ionization detector, a Hewlett-Packard HP 7673A automatic injector, and a VF5-ms 30 m \times 0.25 mm \times 0.25 mm capillary column (Varian), using nitrogen as the carrier gas at a flow rate of 1 mL/min. The injections into the GC system were performed in the splitless mode, and the injector temperature was 300 °C. The oven temperature was held at 50 °C for 2 min, linearly increased to 180 °C by 30 °C/min and then by 8 °C/min to 300 °C, where it was held for 5 min. The detector temperature was 310 °C.

2,2, Binaftyl was added to all the standards and sample extracts before injection as a volumetric internal standard. PAHs were quantified by comparing their peak areas to those of the internal standard and the PAH external standards.

GC/MS Analysis. Final analyses were performed using an HP 5890 (Agilent Technologies, Palo Alto, CA) gas chromatograph connected to a FinniganMAT TSQ 7000 mass spectrometer (ThermoFinnigan, San Jose, CA), with a VF5-ms 30 m \times 0.25 mm \times 0.25 mm capillary column and nitrogen as the carrier gas at a flow rate of 1 mL/min. Samples were injected via a PTV injector in the splitless mode programmed to hold 100 °C for 2 min and then increase the temperature by 700 °C/min to 310 °C. The oven temperature was held at 65 °C for 2 min, linearly increased by 30 °C/min to 180 °C, then 8 °C/min to 300 °C, which was held for 6 min. The temperature of the transfer line was 320 °C.

The MS was operated in electron ionization mode (EI) with single ion monitoring of the molecular ions for all the PAHs. The electron energy was 70 eV, and the filament current was 400 μ A. The temperature at the ion source was 150 °C. A mix of deuterated PAH standards was added to all the external standards and sample extracts before injection. PAHs were quantified by comparing their peak areas to those of the internal standard and the PAH external standards.

Membrane Stability. The major limitation of the suggested approach is the stability of the SPE membrane materials under the harsh conditions required for the DSWE of low-polarity compounds (see Table 1). According to previous experiments and reports,^{47–49} the integrity of Empore disk SPE membranes can

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Table 1. Physical–Chemical Properties Measured at 25 °C of Polycyclic Aromatic Hydrocarbons (from Reference 21)

analyte	MW (amu)	vapor pressure (mmHg)	water solubility (mg/L)	log <i>P</i>	log <i>K</i> _{ow}
phenanthrene	178.2	6.8×10^{-4}	1.20	4.45	4.15
anthracene	178.2	1.75×10^{-5}	0.076	4.45	4.15
fluoranthene	202.3	5.0×10^{-6}	0.23	4.90	4.58
pyrene	202.3	2.5×10^{-6}	1.20	4.45	4.15
benz[<i>a</i>]anthracene	228.3	2.2×10^{-8}	0.010	5.61	5.30
chrysene	228.3	6.3×10^{-7}	2.8×10^{-3}	5.16	5.30
benzo[<i>b</i>]fluoranthene	252.3	5.0×10^{-7}	1.2×10^{-3}	6.04	5.74
benzo[<i>k</i>]fluoranthene	252.3	9.59×10^{-11}	7.6×10^{-4}	6.06	5.74
benzo[<i>a</i>]pyrene	252.3	5.6×10^{-9}	2.3×10^{-3}	6.06	6.74
indeno[1,2,3- <i>cd</i>]pyrene	276.3	1.0×10^{-10}	2.2×10^{-5}	6.58	6.20
benzo[<i>ghi</i>]perylene	276.3	1.03×10^{-10}	2.6×10^{-4}	6.50	6.20
<i>n</i> -octane ^a	114.2	126.4	2.6×10^{-1}	5.01	4.10
<i>n</i> -tritriacontane ^a	464.89	1.01×10^{-8}	2.6×10^{-8}	18.29	7.00

^a Values calculated using Advanced Chemistry Development (ACD/Labs) software version 9.04 for Solaris.

be compromised by subcritical water at very high temperatures. Thus, before selecting a specific type of membrane, stability tests were performed using a range of possible materials.

The SDB-RPS and SDB-XC poly(styrene divinylbenzene) copolymer-based Empore membrane showed good resistance to the experimental conditions. However, it also strongly retained high-molecular mass PAHs, resulting in much lower recoveries (around 30%) under the experimental conditions required for selective extraction of the aromatic hydrocarbons. Thus, this type of SPE membrane, although likely to be very useful for the selective extraction of more polar compounds, was not further investigated for the dynamic extraction of PAHs.

Silica-based stationary phases also have well-known limitations due to the risks of silica hydrolysis. Use of basic aqueous solutions or higher temperatures than approximately 80 °C may compromise, to varying extents, the stability of any silica-derivatized stationary phase. In our stability tests, the first symptom of membrane degradation was white opalescence at the water extract/hexane interface.

Experiments were performed in order to investigate the membranes' stabilities during the DSWE process at two different pressures: 15.0 and 5.5 MPa. In the experiments at 15.0 MPa, in which membranes were extracted at a temperature of 250 °C and flow rate of 1 mL/min after the washing step, fractions of the water extract were collected every 5 min and extracted with hexane. The resulting interfaces of the first three fractions, corresponding to the equilibration time and the first 10 min of extraction, appeared to be transparent. However, white opalescence could be perceived in the fourth fraction (from 10 to 15 min) and significant amounts of hydrolyzed stationary phase were observed in subsequent fractions. The possibility of shortening the extraction time was also investigated, by setting a water flow rate of 2 mL/min and collecting the same water volumes as in the previous experiment. No evidence of membrane degradation was observed during the first 12 min when Empore SPE membranes were extracted under these conditions.

The possibility of using lower pressure to avoid membrane decomposition was also assessed, by reducing the pressure to 5.5 MPa (still above the critical point and thus sufficient to ensure that the water remained in a liquid state) throughout the entire extraction procedure. These milder extraction conditions resulted in less decomposition. However, in order to attain the same extraction yields for the higher MW PAHs obtained at 15.0 MPa, a slightly larger volume of water was required. In previous investigations at constant temperature the solubility in water of benzo[*a*]pyrene has been found to increase with increasing pressure.⁵⁰ In our experiments, the efficiency of extracting PAHs from membranes spiked with standard solutions was reduced at the lower pressure, which can be attributed to increases in their log *P* values. However, the higher efficiency obtained in the extraction of PM at 15.0 MPa can be explained with the desegregation of particulate matter occurring at higher pressures and assisting the extraction of incorporated particles.

Optimization of the Extraction Conditions: Effects of Temperature. Despite the limitations associated with membrane stability, the possibility of using temperatures higher than 250 °C was intensively investigated. To study the effects of the temperature during the DSWE procedure on the recoveries of PAHs with MW higher than 270 amu, membranes were spiked with the "urban dust" standard reference material and extracted at 2 mL/min for 12 min at different temperatures. In experiments at 275 °C, the recovery of some of the high-MW PAHs was found to be higher than at 250 °C. However, the use of such conditions resulted in the extraction and elution of significant amounts of alkanes and other less soluble compounds, compromising the accuracy of the determinations of the target analytes. Therefore, an experiment was carried out in which analytes were extracted with two temperature steps (250 °C from 0 to 6 min, increasing to 275 °C from 6 to 12 min) in an attempt to reduce the amount of coextracted compounds. No improvements in recoveries were observed, but the stability of the SPE membrane was compromised, causing material to bleed from the extraction cell.

Effects of Water Flow Rate. To assess the effects of the water flow rate on the extraction efficiency, membranes spiked with the certified reference material were extracted in experiments in which the temperature and pressure were kept constant but the water flowrate was varied, at 0.3, 1, and 2 mL/min. The same total water volume (18 mL) was collected in all the extractions. Under these conditions, the extraction times for each experiment were 60, 18, and 9 min, respectively.

Since the increase in the water flow rates did not adversely affect the system's efficiency, while both increasing the rapidity of the extraction and reducing the possibility that some of the analytes could be degraded, the maximal flow rate that could be applied while maintaining the pressure stably above 5.0 MPa (2 mL/min with the BPR used in our system) was considered to be the most suitable.

RESULTS AND DISCUSSION

Collection of Very Fine Particles and Semivolatile Compounds. The significance of the health risks posed by very fine PM was recently highlighted in the revised version of the national ambient air quality standards (NAAQS) set by the U.S. EPA, in

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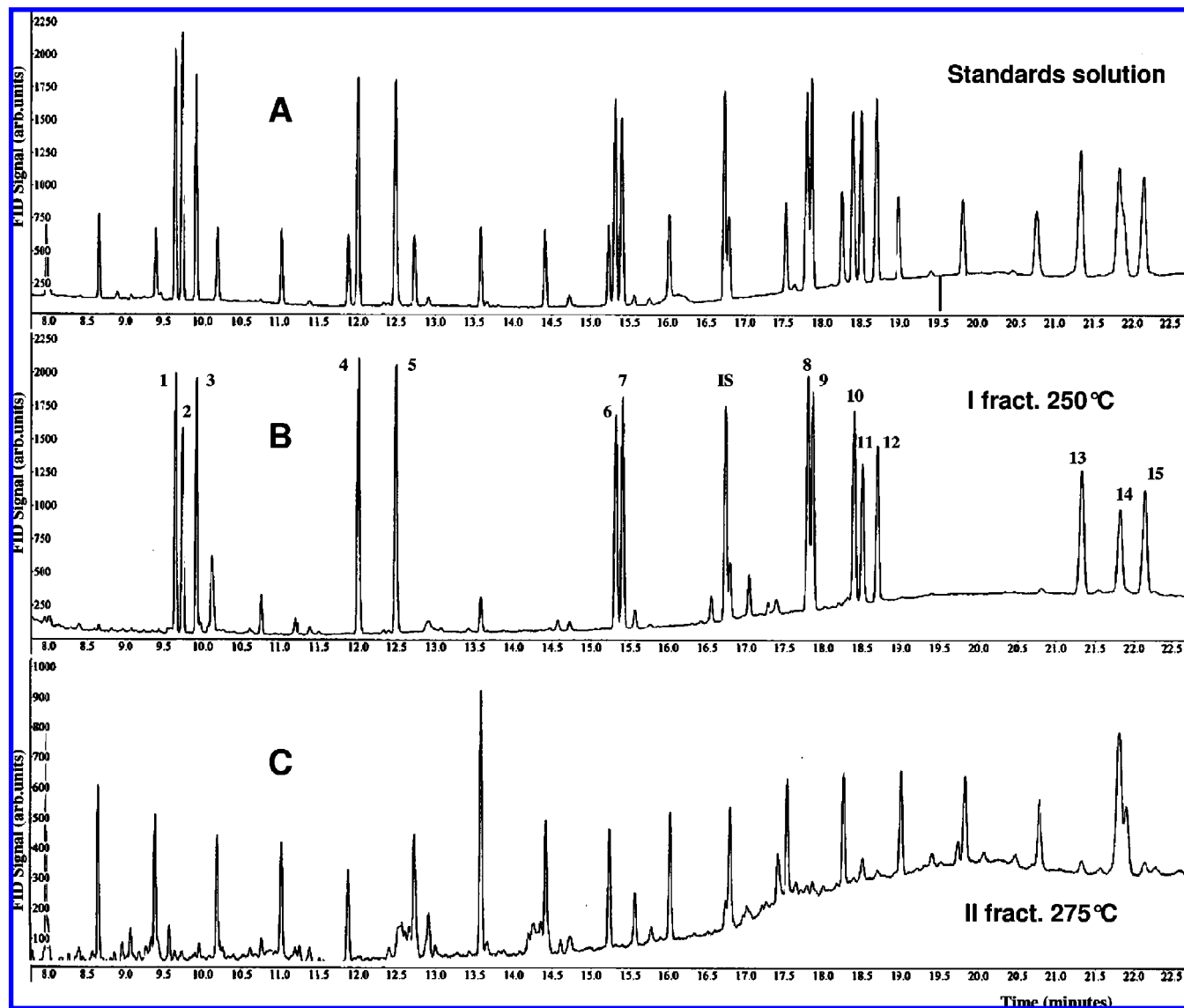


Figure 2. GC-FID chromatograms showing the selective extraction obtained by applying DSWE at different temperatures to C8 Empore SPE membranes spiked with a mixture of 16 PAHs and 26 alkanes (C_8 – C_{33}). (A) Chromatogram obtained from the standard solution containing PAHs and *n*-alkanes. (B) Chromatogram obtained from a spiked membrane extract using DSWE at 250 °C: 1, acenaphthylene; 2, acenaphthene; 3, fluorene; 4, phenanthrene; 5, anthracene; 6, fluoranthene; 7, pyrene; 8, benz[*a*]anthracene; 9, chrysene; 10, benzo[*b*]fluoranthene; 11, benzo[*k*]fluoranthene; 12, benzo[*a*]pyrene; 13, indeno[1,2,3-*cd*]pyrene; 14, dibenz[*a,h*]anthracene; 15, benzo[*ghi*]perylene; IS, 2,2'-binaphthalene. (C) Chromatogram obtained from the analysis of the second fraction at 275 °C.

which $PM_{2.5}$ was listed as one of six principal (or “criteria”) pollutants.⁵¹ PM_{10} was revoked as a quality standard parameter due to the lack of evidence linking health problems to long-term exposure to coarse particle pollution. Since concern is now focused on very fine particles, in order to verify the trapping efficiency of Empore membranes, a condensation particle counter was placed downstream of the trap in our study, allowing even low numbers of particles passing through the tested filtration device to be detected. Experiments using a SMPS demonstrated that aerosols with particle sizes ranging between 10 and 800 nm diameter are virtually completely retained by Empore disk membranes. No evidence of particles passing through the membranes was observed even after prolonged sampling (24 h) at relatively high flow rates (20 L/min). Empore SPE membranes (500 μ m thick) consist of

octyl-derivatized porous silica particles (size 12 μ m, pore size 60 Å, carbon 15.5%) held together within an inert matrix of polytetrafluoroethylene (90% sorbent: 10% PTFE, by weight). The very large, porous, “greasy” surface of the alkyl-derivatized silica is probably responsible for the efficient trapping of nanoparticles. A major advantage of using this type of sampling device is the scope it offers for avoiding losses of semivolatile compounds, even when large sample volumes or high vapor temperatures are used.³⁰ Furthermore, the samples can be conveniently and safely stored by packing the membrane in the extraction cell just after the sampling.

Fractionated Extraction of Organic Compounds from Particles Embedded in SPE Material Using DSWE. After sampling, the membrane (together with the sampled particles) is packed in an extraction cell similar to a chromatographic column. Thus, the matrix to be extracted (PM) is embedded in SPE

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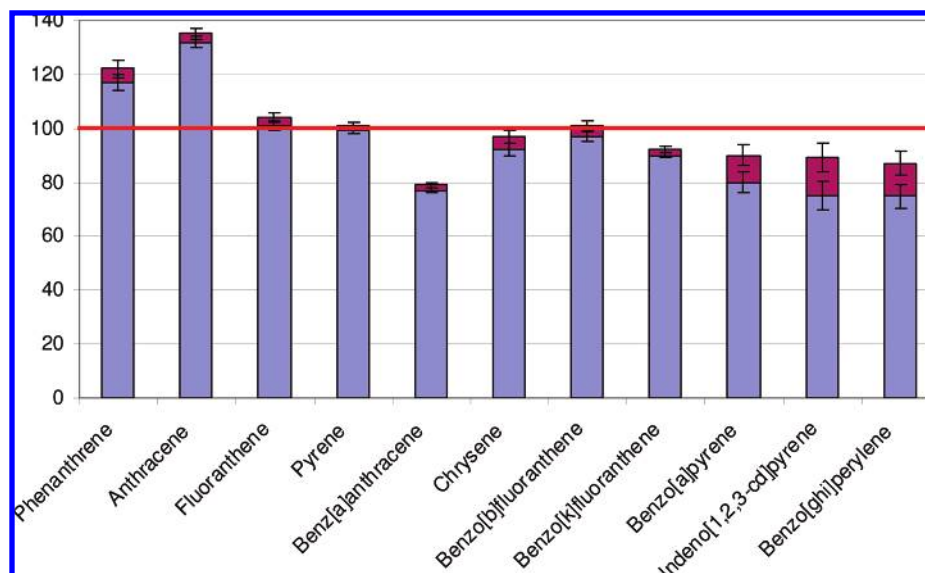


Figure 3. Elution curve and relative recoveries from Empore membranes spiked with 1.3–2 mg of NIST standard reference material (SRM 1649a) after two washing steps (80 °C and 130 °C) and extracted at 250 °C. Light bars, first 18 mL fraction; darker bars, second 18 mL fraction. Error bars are \pm standard deviation.

Table 2. Optimized Extraction Procedure Description

time (min)	description	T (°C)	P (bar)	P1 flow rate (mL/min water)	P2 flow rate	N_2	solvent selector
0	system is liquid filled and pressurized	25	≈ 1		off	off	water
2	DSWE washing (step one)	80	55	2	off	off	water
12	DSWE washing (step two)	130	55	2	off	off	water
22	DSWE extraction process	250	55	2	off	off	water
40	water removal			off	off	on	N_2
41	tubing rinsing			off	on	off	hexane

material in an analogous fashion to materials in matrix solid-phase dispersion (MSPD),^{52,53} which facilitates efficient selective extraction by suitable solvents.

In this study, instead of using different organic solvents, the polarity of the extracting phase was adjusted by changing the temperature of pure water. Selective extraction was obtained by pre-washing the samples using water at relatively low temperature (80 °C) in order to remove the so-called water-soluble organic carbon fraction. Even cleaner extracts were obtained by performing a second washing at 130 °C to remove further organic compounds, with intermediate polarities between those of the compounds in the first fraction and PAHs. Finally, the temperature was increased sufficiently to selectively desorb PAHs, while retaining aliphatic compounds and higher molecular mass compounds in the cell.

As analytes move through the column after they have been desorbed from the matrix (PM), their progress is affected by reverse-phase chromatographic interactions with the C8 SPE material in the extraction cell. Similarly to subcritical water chromatography (SWC), decreasing the dielectric constant of the water by increasing its temperature results in the elution of less polar and higher MW organic compounds. For this reason, prior to the PM extraction experiments, in order to investigate the elution parameters of aromatic and aliphatic alkanes from Empore

C8 material, membranes were spiked with standard solutions. Liquid-spiked membranes were extracted under various conditions in terms of flow rate, temperature, and volume of extraction phase. As expected, the elution order and kinetics were consistent with results obtained by other authors who have used SWC and SWE⁵⁴ with reversed phase columns and the physicochemical properties of the compounds (Table 1). Under these conditions, due to the lower solubility of aliphatic compounds in SW, aromatic hydrocarbons can be selectively eluted. GC-FID chromatograms obtained from analyses of a spiked membrane extract and the standard solution used to spike the membrane, illustrating the selectivity of the extraction under the optimized conditions, are presented in Figure 2.

Influence of Water Volume. In order to evaluate the elution kinetics of the analytes, membranes spiked with the certified reference material were extracted with 36 mL of water at 250 °C and a flow rate 1 mL/min for collecting fractions. As shown in Figure 3, most of the extracted analytes eluted in the first 18 mL. As expected, in the first fraction, the extraction efficiency was significantly better for PAHs with low molecular masses than for those with higher molecular masses. Doubling the water volume resulted in only small improvements in the recoveries of the heaviest PAHs. The high-molecular mass PAHs, from benzo[b]-fluoranthene to benzo[ghi]perylene, are challenging compounds

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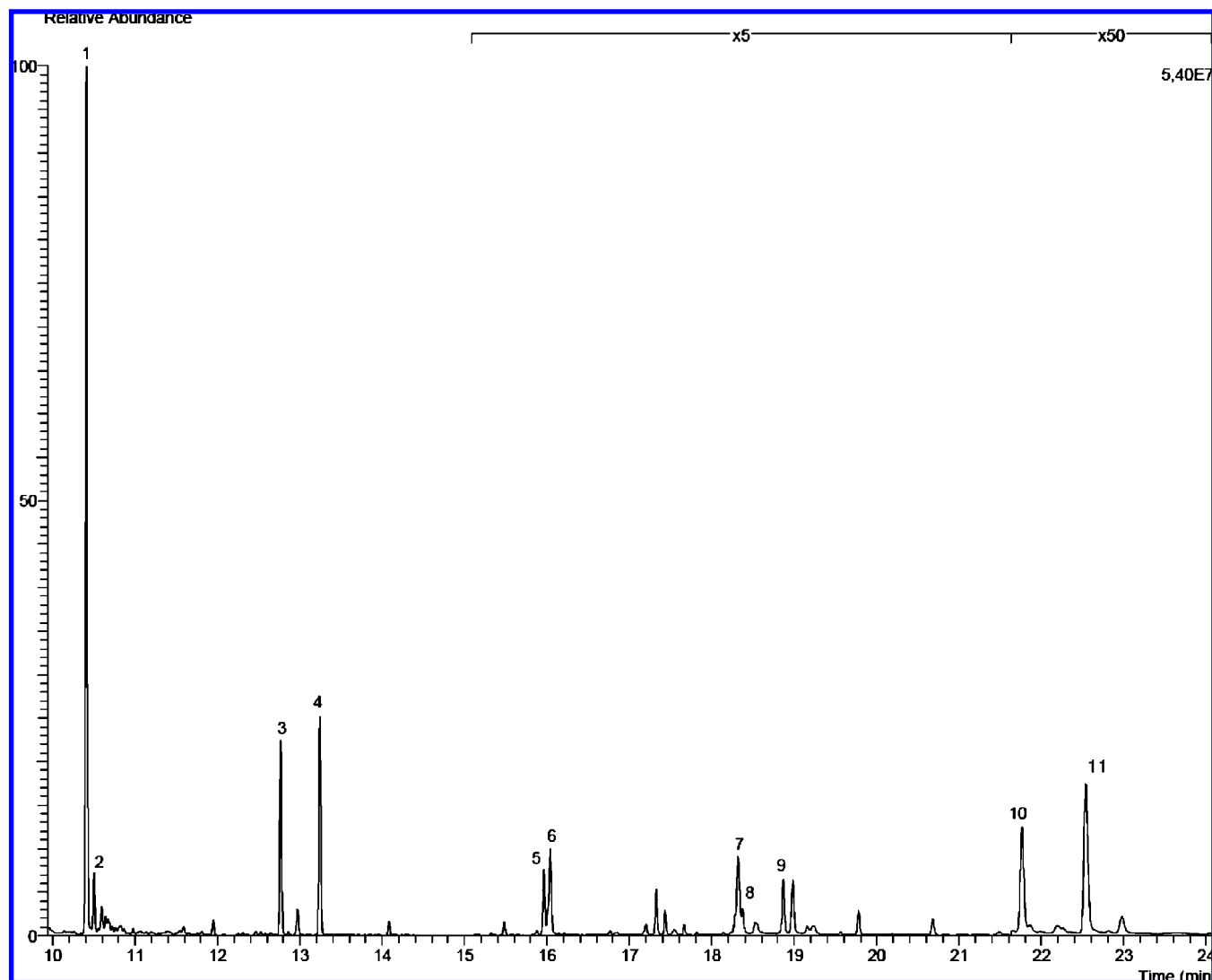


Figure 4. GC/MS chromatograms of a 0.879 m³ air sample collected at roof level in the center of Rome (Italy). Measured concentrations in ng/m³: 1, phenanthrene 467; 2, anthracene 22; 3, fluoranthene 125; 4, pyrene 139; 5, benz[*a*]anthracene 17; 6, chrysene 32; 7, benzo[*b*]fluoranthene 25; 8, benzo[*k*]fluoranthene 10; 9, benzo[*a*]pyrene 30; 10, indeno[1,2,3-*cd*]pyrene 19; 11, benzo[*ghi*]perylene 31.

Table 3. Method Performances in the Optimized Conditions at Three Different Amount of PM

analyte	1.3–2 mg		4.4–4.9 mg		9.7–11 mg		overall ^b			
	recovery ^a (%)	CV ^a (%)	recovery ^a (%)	CV ^a (%)	recovery ^a (%)	CV ^a (%)	recovery (%)	CV (%)	<i>R</i>	MDL (pg/m ³)
phenanthrene	117	6.1	121	7.7	109	6.6	116	8.0	0.9933	5.0
anthracene	132	4.1	149	4.0	134	5.4	138	8.9	0.9956	6.0
fluoranthene	101	3.5	106	9.8	98	5.6	101	6.9	0.9938	4.0
byrene	99	2.1	109	8.5	102	5.8	103	7.0	0.9948	4.0
benz[<i>a</i>]anthracene	77	1.5	81	6.0	84	2.8	81	4.6	0.9982	4.5
chrysene	92	4.6	96	1.0	95	1.6	95	2.9	0.9996	4.0
benzo[<i>b</i>]fluoranthene	97	3.8	88	13.9	86	11.2	90	10.6	0.9805	20
benzo[<i>k</i>]fluoranthene	90	2.2	79	7.5	74	1.6	81	8.3	0.9971	30
benzo[<i>a</i>]pyrene	80	7.9	70	1.2	86	14.1	79	10.6	0.9698	39
indeno[1,2,3- <i>cd</i>]pyrene	75	10.7	67	3.5	59	5.0	67	9.2	0.9903	29
benzo[<i>ghi</i>]perylene	75	8.8	76	7.0	68	3.6	73	7.0	0.9933	26

^a *n* = 3. ^b *n* = 9.

to extract with SWE. Low recoveries of these compounds have been previously reported by other authors who have assessed different methods in static conditions, and are presumably due to the solubility of these compounds being orders of magnitude lower than those of the lighter PAHs.⁵⁵ The results of this experiment

corroborate the finding that a key determinant of the efficiency of the dynamic extraction process is the temperature.

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Optimized Conditions. On the basis of this evaluation, a set of conditions (Table 2) were identified that seem to ensure effective, reproducible, and selective extraction of the PAHs. Additional attention was paid to the washing steps. In order to exploit the selectivity of DSWE, the protocol was adjusted to collect two fractions, one of "water-soluble" and one of compounds with intermediate solubilities between those of the polar organic carbon compounds and the PAHs, to be evaluated in further studies. After the aromatic hydrocarbon compounds were washed, they were extracted in a fraction obtained by eluting with 35 mL of water at 250 °C, 5.5 MPa, and a flow rate of 2 mL/min. These conditions resulted in high recoveries and insignificant decomposition of the membranes.

Method Performance. In previous studies, SWE has been shown to be an ideal technique for extracting polar compounds from various matrixes, offering several advantages in terms of performance, cost, and environmental compatibility. Because of their low polarity, using SWE for extracting PAHs from PM presents a stiff challenge, since they are probably close to the physicochemical limits of compounds that can be extracted using this approach. On the other hand, the attractive potential of this technique for selective elution by applying DSWE to SPE membranes warrants attempts to extend the applicability of this technique to its extreme limits in terms of the MW and polarity of the target analytes. Overall performance parameters are presented in Table 3. As expected, the recoveries were lower for high-molecular mass analytes than for lighter analytes. Although the recoveries of recalcitrant analytes could be increased by using higher temperatures, 250 °C and 5.5 MPa were the preferred temperature and pressure in order to separate the PAHs from aliphatic compounds efficiently while preserving the membrane's stability. The elution of larger molecules and lower polarity compounds could be enhanced using the same cell (similar to a conventional MSPD column) and lower polarity solvents. The use of more robust SPE material could also extend the potential applicability of this approach and allow recoveries to be improved by using higher temperatures and pressures. The linearity of the method, with respect to sample quantities, was evaluated by extracting different amounts of NIST-certified urban dust particulate matter. Results presented in Table 3 confirm the efficacy (and linearity) of the selected conditions, at least for amounts of PM that are likely to be sampled in routine measurements. The efficacy of the presented method was verified by collecting airborne PM from a site with heavy traffic in a large European city, Rome (Figure 4). The presence of relevant amounts of PAHs demonstrates the risks still arising from PM in urban areas and the need to reduce emissions from heating systems, propulsion

engines, and vehicles. In addition, it may be possible to detect variations in the quality of the fuels used, in terms of emissions, from analyses of the composition of the particulate material using this approach.

CONCLUSIONS

Empore disk SPE membranes can efficiently trap nanoparticles and fine particulate matter from very large air samples. These characteristics and their ability to trap semivolatile and some volatile compounds suggest that they can be successfully used as sampling devices for collecting environmental air samples and investigating the chemical composition of PM.

In addition, the results presented here demonstrate the potential of DSWE for selectively extracting PAHs from PM trapped on C8 Empore SPE membranes using liquid water at 250 °C, 5.5 MPa, and a flow rate of 2 mL/min. The most influential variables in the DSWE method are the temperature and the water volume used in the extraction, while the flow rate, extraction time, and pressure each have minor influences on the process. Slight improvements in recoveries were observed using higher pressure. The highest feasible flow rates were selected in order to reduce the total extraction time and avoid degradation of the SPE membrane. The optimal DSWE conditions are essentially limited by the resistance of the material and fluid dynamic properties of the extraction apparatus. Acceptable recoveries were obtained for most of the selected analytes using 35 mL of pure water, even from relatively large amounts of PM. The results demonstrate that targeted fractions of the components can be simply and rapidly eluted using a more environmentally friendly procedure than conventional techniques.

The presented methodology represents an alternative approach for sampling and extracting airborne particulate matter, which could be greatly improved if the stability of the available SPE membrane materials could be increased.

ACKNOWLEDGMENT

The authors thank Håkan Carlsson, Roger Westerholm, and Christoffer Bergvall for helpful discussions and Lena Elfver and Davide Tamburro for their assistance in the initial experiments and real sample collection. Preliminary results have been presented at the Pittsburgh Conference (Pittcon 2005) Orlando, FL, February 27–March 4, 2005.

Received for review October 17, 2007. Revised . Accepted February 12, 2008.

AC7021458