

Efficient screening method for determination of polycyclic aromatic hydrocarbons (PAHs) in airborne particles. Application in real samples of Santiago–Chile metropolitan urban area

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Abstract

A rapid analytical approach for determination of polycyclic aromatic hydrocarbons (PAHs) present in real samples of particulate matter (PM10 filters) was investigated, based on the use of water under sub critical conditions, and the subsequent determination by GC-MS (SIM). The method avoids the use of large volumes of organic solvents as dichloromethane, toluene or other unhealthy liquid organic mixtures which are normally used in time-consuming conventional sample preparation methods. By using leaching times < 1 h, the method allows determination of PAHs in the range of ng/m³ (detection limits between 0.05 and 0.2 ng/m³ for 1458 m³ of sampled air) with a precision expressed as RSD between 5.6% and 11.2%. The main idea behind this approach is to raise the temperature and pressure of water inside a miniaturized laboratory-made extraction unit and to decrease its dielectric constant from 80 to nearly 20. This effect allows an increase in the solubility of low polarity hydrocarbons such as PAHs. In this way, an extraction step of a few minutes can be sufficient for a quantitative extraction of airborne particles collected in high volume PM10 samplers. Parameters such as: extraction flow, static or dynamic extraction times and water volume were optimized by using a standard reference material. Technical details are given and a comparison using real samples is made between the conventional Soxhlet extraction method and the proposed approach.

The proposed approach can be used as a quantitative method to characterize low molecular PAHs and simultaneously as a screening method for high molecular weight PAHs, because the recoveries are not quantitative for molecular weights over 202. In the specific case of the Santiago metropolitan area, due to the frequent occurrence of particulate matter during high pollution episodes, this approach was applied as an efficient short-time screening method for urban PAHs. Application of this screening method is recommended especially during the winter, when periods of clear detriment of the atmospheric and meteorological conditions occur in the area.

Keywords: Polycyclic aromatic hydrocarbons; Environmental trace analysis; Screening method; Particulate matter; Ambient air

1. Introduction

Recent investigations in the field of air pollution, as well as a large set of collected data, have consistently shown that polycyclic aromatic hydrocarbons (PAHs) remain as a concern, due to their adverse effects on human health, especially the carcinogenic properties

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attributed to many compounds of this class (Lee et al., 1981). Therefore, countries such as Japan (Environmental Agency, Japan 1997) have already included some relevant PAHs in their continuous air quality monitoring networks, and focus on the surveillance of specific target/tracer compounds (as benzo[*a*]pyrene) in order to control the emission and release of these pollutants into the environment.

The establishment of a database for PAHs requires a measurement technique which can be as simple as possible to reduce the cost per analysis in time and materials, and to cover a concentration range of low parts per 10^9 ppb in ambient air. Furthermore, the sensitivity should be high enough to properly identify the most toxic components. Most of the methods developed for the analysis of PAHs are based on time-consuming Soxhlet extraction procedures which are normally difficult and involve the use of large quantities of toxic organic solvents such as dichloromethane, acetone, hexane and toluene (Catoggio et al., 1989; Peltonen and Kuljukka, 1995; Gogou et al., 1988; König et al., 1983; US-EPA, 1988). This fact is one of the reasons which lead to the rapid development of sub- and supercritical fluid extraction methods (SFE) applied to analytical procedures (Hawthorne et al., 1994; Crescenzi et al., 2000; Hageman et al., 1996; Yang et al., 1995; Clement et al., 1999). In this regard, one of the most common fluid solvents, carbon dioxide (CO_2), is widely used to extract organic compounds. However in the case of PAHs, this solvent is not recommended because it provides a poor ability to displace this kind of pollutant from the active matrix sites (Lagadec et al., 2000). Therefore, instead of CO_2 , water has been tested in the present study to extract organic compounds from particulate matter, despite that the fact that PAHs do not have high water solubility in normal ambient conditions. Actually, PAHs associated with particulate matter have been reported to have solubility in ambient water, which rapidly decrease with molecular weight from $32 \mu\text{g/ml}$ for naphthalene (C_{10}H_8) to $3 \times 10^{-4} \mu\text{g/ml}$ for benzo[*g,h,i*]perylene ($\text{C}_{22}\text{H}_{12}$) (Hawthorne et al., 1994).

An interesting and promising approach for low ppb measurements of organic pollutants has been described by Hawthorne et al. (1994) based on the use of sub- and supercritical water extraction as a simple method for extraction of organics from environmental solids, including certified reference materials for PAHs in particulate matter. The aim of the present study was to investigate the possibility of implementing such an approach as a screening method to apply to real world samples to characterize PAHs present in the organic fraction of a particulate matter filter, in order to evaluate the air quality in urban areas. By using a miniaturized oven device, instead of a gas chromatograph oven, the original method can be simplified

considerably. The heating transfer between the oven and the column extractor becomes more efficient and the required temperature is reached faster, allowing a shorter extraction procedure. In fact, as soon as the optimal oven temperature is reached, the column with the particulate matter filter loaded inside can be located inside the miniaturized oven device and the extraction can be started. In this context, the extraction efficiency of water under sub critical conditions was combined with a laboratory-made small aluminum oven extractor which allows the dynamic extraction of PAHs from airborne particles collected on PM10 filters. After optimization of the extraction parameters, the method was applied to samples of PM10 filters collected from the downtown Santiago metropolitan area, and the results compared with the conventional Soxhlet extraction method.

2. Experimental

2.1. Reagents

All chemicals used were of analytical-reagent grade unless stated otherwise. De-ionized water (NANOpure ultrapure water system; Barnstead, Dubuque, IA, USA) was used throughout. Working standard solutions of PAHs were prepared by dilution of an EPA 610 polynuclear aromatic hydrocarbons mix containing concentrations between 100 and 2000 $\mu\text{g/ml}$ (SUPELCO Park, Bellefonte, PA, 4-8743). Dichloromethane (GC-MS/pesticides grade analysis, Fisher Scientific, Fair Lawn, New Jersey, USA) was used as final extractant. Certified standard reference samples used to optimize the subcritical water proposed method, were obtained from the US National Institute of Standard and Technology (NIST), urban air particulate matter (NIST "urban dust" SRM 1649a).

2.2. Instruments and apparatus

The schematic drawing of the extraction unit is shown in Fig. 1. All tubes ($\frac{1}{16}$ " $\frac{1}{8}$ " OD) were made from SS-306 stainless steel. Connections were made using Swagelok fittings. The following valve type was employed: 2-way Whitney SS-needle valve, (5000 psi allowed pressure).

The extraction chamber consisted of a laboratory made oven ($28 \times 12 \times 5 \text{ cm}^3$ aluminum block with controlled temperature). Inside the chamber, a pre-heated coil (2 m stainless steel tube SS-316, $\frac{1}{16}$ ", 0.1 mm ID) was located to keep the programmed temperature and was followed by the extraction cell (a 12 mm ID empty HPLC column, Supelco, Bellefonte PA, USA). The deionized water for the extraction was pumped using a HPLC pump (model WatersTM 600 Pump) operated in the constant pressure mode. For extraction,

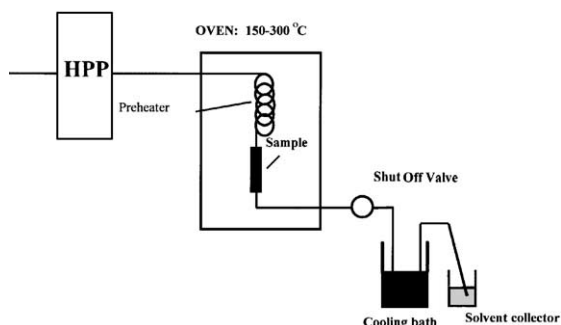


Fig. 1. Subcritical water extractor. HPP, high pressure pump.

the working range of pressure inside the system was kept between 1200 and 1800 psi.

The PAH quantitation was conducted using a gas chromatograph Hewlett-Packard model 6890 HRGC coupled to a 5973 MSD, equipped with a 30 m HP-5MS column (0.25 μm film thickness, 250 μm ID, Hewlett Packard).

2.3. General procedure

The PM10 filters containing real samples of particulate matter were divided into two parts using ceramic scissors. After that, each part of the filter was extracted separately according to the following procedures.

2.3.1. Subcritical water extraction

One half of the filter, or firstly the 200 mg of standard reference material used to optimize the variables, was previously loaded into an extraction cell located inside the aluminum chamber—oven extractor. All valves were dismantled before use, cleaned with methanol, and heated to 110°C in a stream of purified He for 2 h. The oven was coupled to a heating device located on the upper part of the chamber and electronically controlled through a thermocouple until to reach 300°C. Then, water was pumped through the system to extract the PAHs from the PM10 filters at a flow rate of 1 ml/min for 50 min. After the sub critical water extraction was done, the PAHs already in the water phase were transferred quantitatively into 25 ml of dichloromethane, then evaporated and concentrated to 1 ml prior its characterization by GC-MS.

2.3.2. Conventional Soxhlet extraction

The other half of the filter was treated using the conventional Soxhlet extraction procedure. A detailed description of the analytical procedure used for extraction, clean up and the analysis of those samples is described previously (US-EPA, 1988). Basically it consist of the extraction procedure of Soxhlet using

Table 1
Selected target ions and qualifier ions used in SIM mode

Compound	Target	Qualifiers
Naphthalene	128	129, 127
Acenaphthylene	152	151, 153
Acenaphthene	154	152, 153
Phenanthrene	178	176
Fluorene	166	165
Anthracene	178	176
Fluoranthene	202	101, 203
Pyrene	202	200
Benzo[<i>a</i>]anthracene	228	226
Chrysene	228	229
Benzo[<i>b</i>]fluoranthene	252	253, 125
Benzo[<i>k</i>]fluoranthene	252	253
Benzo[<i>a</i>]pyrene	252	253, 125
Indeno[1,2,3- <i>c</i> , <i>d</i>]pyrene	276	138, 227
Dibenzo[<i>a,h</i>]anthracene	278	139, 279
Benzo[<i>g, h, i</i>]perylene	276	277

dichloromethane as the extraction solvent, then the extract, after evaporation in a rotaevaporator, is cleaned using a chromatographic column with activated silica-gel. Finally, the extract is concentrated in a N_2 stream to 1 ml then characterized by GC-MS. The final determination by GC-MS was carried out according to the following parameters:

Carrier gas: Helium (1 ml min⁻¹, constant flow)
 Temp. program: 40°C (2 min), 40–140°C (20°C/min)
 280°C (15 min), 280–300°C (10°C/min), 300°C (2 min).
 Injection volume: 1 μl (splitless)
 Injector temp.: 250°C

The MS transfer line was held at 280°C and the quantitations were based on calibration with standard PAHs using the mass spectrometric parameters (selected ion monitoring, SIM mode) shown in Table 1.

Peak identification of PAHs was based on the retention times and full scan spectra of the standards and particulate matter filter samples. Quantitation was based on SIM mode for the molecular ion of each analyte.

2.3.3. Samples

The PAHs in airborne particulate matter were collected on 20 \times 25 cm quartz fiber filters, mounted in a High Volume Air Sampling System (Andersen Inc., USA). Samples were collected for a 24 h period at the roof of a 15 m high building in downtown Santiago (Computer Center, Faculty of Physical Sciences and Engineering, University of Chile). The sampling flow was 1.013 m³/min, and the total volume sampled was

1458 m³. After sampling, the samples were stored in a refrigerator at 4°C prior to analysis.

3. Results and discussion

The use of water as a solvent for extraction of low polarity compounds has been based mainly on its properties provided under subcritical conditions. Low polarity compounds such as anthracene, chrysene and perylene each have solubilities ca. 20 000-fold higher in water at 200°C than at 25°C (Hawthorne et al., 2000). The strong dependence of the dielectric constant with the temperature, also reduces viscosity and surface tension, that makes water an effective solvent for leaching a number of organic compounds that have a broad spectrum of polarity in solid samples (Crescenzi et al., 2000). On the other hand, water does not exhibit toxicity-associated problems like organic solvents commonly used in the conventional sample preparations. Further, subcritical water conditions can be easily achieved with low-cost laboratory devices.

Normal extraction apparatus used for subcritical water extraction involve the use of a gas chromatograph oven to carry out the leaching process (Hawthorne et al., 2000, 1994; Crescenzi et al., 2000; Hageman et al., 1996; Yang et al., 1995; Clement et al., 1999). In the present approach, the situation is simpler by using a laboratory-made miniaturized device which can easily accommodate the extraction manifold (Fig. 1).

The main parameters for subcritical water extraction were first optimized, using the Standard Reference Material NIST 1649a urban dust by following as representative compounds the following PAH constituents: phenanthrene, anthracene, fluoranthene, pyrene, benzo[*a*]anthracene, chrysene, Benzo[*b*, *j*, *k*]fluoranthene, benzo[*a*]pyrene and benzo[*e*]pyrene.

3.1. Effect and optimization of variables

3.1.1. Effect of temperature on PAHs extraction

The effect of temperature for PAH extraction was checked using different temperatures in the range between 150°C and 300°C. An extraction temperature higher than 300°C was rejected because there is evidence of molecular re-arrangements for high molecular weight hydrocarbons. As shown in Fig. 2, the best efficiency was found at 300°C for some representative compounds.

3.1.2. Effect of time on PAHs extraction

The effect of static time in the extraction efficiency appears to be negligible. Many tests were done to check this effect, however, there was no clear evidence that showed the importance of this effect. On the other hand, the dynamic time on the extraction efficiency was found to be important. As shown in Fig. 3, for two represen-

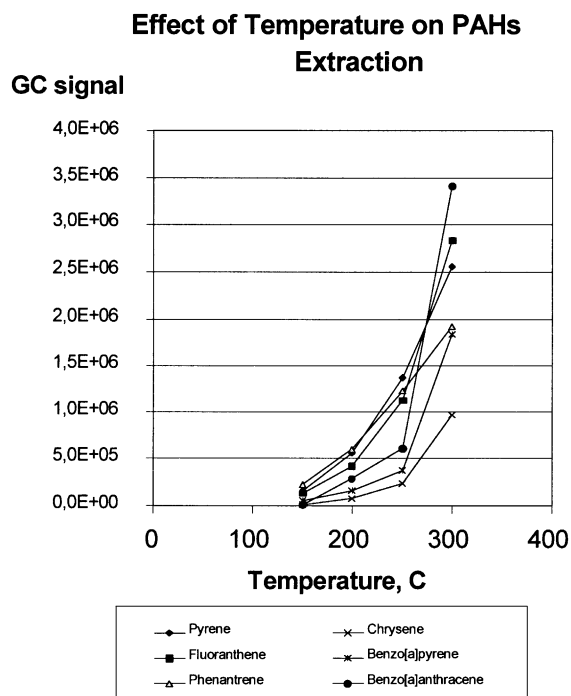


Fig. 2. Effect of temperature on PAHs extraction.

Effect of the Dynamic Time on the Extraction of PAHs

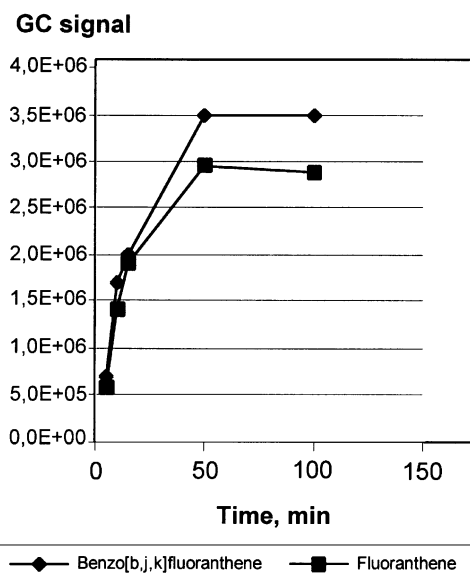


Fig. 3. Effect of the dynamic time on the PAHs extraction.

tative compounds, from 5 to 50 min at a flow rate of 1 ml min⁻¹, the extraction increased, reaching the best efficiency in the range 40–50 ml of collected volume. This

Table 2
Comparison of water subcritical extraction of individual PAHs presents in urban air particulate matter (SRM 1649a)

Compound	Concentration certified by NIST ^a (mg/kg)	Concentration obtained by water extraction (mg/kg)	% Recovery
Phenanthrene	4.10	5.66	138
Anthracene	0.43	0.40	93
Fluoranthene	6.50	6.62	102
Pyrene	5.30	5.24	99
Benzo(<i>a</i>)anthracene	2.21	1.51	68
Chrysene	3.05	2.44	80
Benzo(<i>b</i> + <i>j</i> + <i>k</i>)fluoranthene	8.40	5.65	67
Benzo(<i>e</i>)pyrene	3.10	2.35	76
Benzo(<i>a</i>)pyrene	2.50	1.43	57

^aTheses data were obtained using Soxhlet extraction method.

effect was performed at an extraction temperature of 250–300°C. The evaporated and then concentrated extracts of 1 ml were finally characterized by GC-MS. The same GC-MS method and chromatographic conditions were applied to the extracts obtained using both methods (Soxhlet and Sub critical water extraction). Finally, the optimal conditions for the sub critical water extraction method were found in the following set up:

Aluminum chamber temperature: 300°C
Dynamic time under extraction: 50 min
Flow rate through the extraction unit: 1 ml min⁻¹

A clear advantage of a dynamic extraction process over the batch static alternative is that, in the first case, the water is cooled outside of the extraction cell avoiding the possibility of re-adsorption of the analytes on the solid matrix. This is an important issue to consider because it has been observed with higher molecular weights PAHs that some partitioning back to the solid occurs (Hageman et al., 1996).

In contrast to other environmental solid matrices, urban particulate matter contains very high concentrations of extractable alkanes in the range C₁₈–C₃₆. The presence of these compounds can make the chromatographic determination of PAHs difficult if a clean up step of the extract is not considered. Fortunately, the selectivity of water as the extractant permits extracts PAHs but not alkanes larger than C₁₈ (Hawthorne, 1994; Hageman, 1996). This fact allows, after the transference of the analytes from the water to dichloromethane, the final organic extracts to be concentrated to 1 ml prior to injection in the GC-MS, without an additional clean up procedure before the injection. In any case, we checked that no interference from the matrix constituents were appreciated by following this procedure. The chromatographic response was the same as previously observed when a clean up of the extract was performed.

Under optimal conditions (see Table 2), the recovery in the standard reference material is over 80% in the case of low molecular weight PAHs (ranging from MW = 128–202), but over molecular weights of 220, the recovery rapidly decreases to 57–80% which agree with previous observation by Hawthorne et al. (1994). The repeatability of the method was assessed by processing six samples of SRM under the optimized conditions. The relative standard deviation (RSD) of the determinations were in the range 5.6–11.2%. Detection limits, calculated by using the 3 σ /n criteria, were between 0.05 to 0.2 ng/m³.

3.2. Analysis of real samples of particulate matter

The results of the present approach were checked against the conventional PAH extraction method, in order to evaluate the efficiency of the proposed method in real samples of suspended particulate matter from Santiago, Chile. Tables 3 and 4 show data with the results. A similar situation as in the analysis of the standard reference material (Table 2) occurs when the real samples were analyzed. In the case with low molecular weight PAHs (ranging from MW = 128–202), like naphthalene, acenaphthylene, acenaphthene, phenanthrene, fluorene, anthracene, fluoranthene and pyrene, the extraction efficiencies obtained for PM10 filter are shown in Table 3. Data for sub critical water conditions (300°C and 50 bar) are quite comparable to the values obtained for the Soxhlet extractions. For most of the PAHs listed, the water extraction gave quite satisfactory quantitative comparability to the Soxhlet extractions. The ratio between Soxhlet to subcritical extraction approach is in a range between 1.01 and 1.23. The single exception is fluorene with 3.05, which could be explained due to the instability of this compound under subcritical conditions. It has been observed that there is a relatively short half-life time of this compound compared with those reported for other PAHs

Table 3

Concentration of individual PAHs present in particulate matter filters (PM-10) collected in downtown Santiago, Chile, extracted by subcritical water and conventional Soxhlet methods

Sample date	Total particle PM-10 ($\mu\text{g}/\text{m}^3$)	Naphthalene		<i>R</i>	Acenaphthylene		<i>R</i>	Fluorene		<i>R</i>	Phenanthrene		<i>R</i>	Anthracene		<i>R</i>	Fluoranthene		<i>R</i>	Pyrene		<i>R</i>
		Water	Soxhlet		Water	Soxhlet		Water	Soxhlet		Water	Soxhlet		Water	Soxhlet		Water	Soxhlet		Water	Soxhlet	
93.08.12	148	0.56	0.66	1.18	0.37	0.44	1.19	0.69	1.09	1.59	1.57	1.99	1.27	0.60	0.62	1.02	1.18	1.45	1.23	2.38	2.36	0.99
93.09.21	120	0.53	0.56	1.06	0.49	0.52	1.08	0.66	1.97	3.00	2.27	2.34	1.03	0.65	0.69	1.06	2.06	2.30	1.12	3.12	3.11	1.00
93.08.19	166	0.42	0.44	1.04	0.30	0.32	1.07	0.29	1.31	4.54	1.32	1.35	1.02	0.45	0.55	1.22	1.01	1.38	1.37	1.73	2.23	1.29
93.09.26	100	0.79	0.60	0.76	0.54	0.59	1.10	0.68	2.10	3.06	2.05	2.29	1.12	0.47	0.58	1.22	1.55	1.87	1.21	2.53	2.66	1.05
	Average			1.01			1.11			3.05			1.11			1.13			1.23			1.08
	SD			0.18			0.06			1.20			0.11			0.10			0.10			0.14
	RSD			17.7			5.08			39.5			10.3			9.19			8.48			13.21

PAHs concentrations are expressed in ng/m^3 .

R: ratio between concentration obtained by Soxhlet extraction to water extraction.

Table 4

Concentration of individual PAHs present in particulate matter filters (PM-10) collected in downtown Santiago, Chile, extracted by subcritical water and conventional soxhlet methods

Total particle PM-10 ($\mu\text{g}/\text{m}^3$)	Benzo[<i>a</i>]anthracene		<i>R</i>	Chrysene		<i>R</i>	Benzo[<i>b</i>]fluoranthene		<i>R</i>	Benzo[<i>k</i>]fluoranthene		<i>R</i>	Indeno[1,2,3- <i>c</i> , <i>d</i>]pyrene		<i>R</i>	Dibenzo[<i>a</i> , <i>h</i>]anthracene		<i>R</i>	Benzo[<i>a</i>]pyrene		<i>R</i>	Benzo[<i>g</i> , <i>h</i> , <i>i</i>]perylene		<i>R</i>
	Water	Soxhlet		Water	Soxhlet		Water	Soxhlet		Water	Soxhlet		Water	Soxhlet		Water	Soxhlet		Water	Soxhlet		Water	Soxhlet	
148	2.10	3.53	1.69	1.06	2.51	2.36	0.98	3.44	3.51	0.89	2.62	2.95	1.67	14.28	8.57	0.16	0.80	4.83	1.33	5.05	3.80	6.65	37.89	5.70
120	3.16	3.78	1.20	3.46	3.82	1.11	4.36	7.62	1.75	3.15	5.56	1.77	7.78	21.47	2.76	6.03	12.72	2.10	4.53	7.89	1.74	22.32	45.05	2.02
166	1.08	1.96	1.81	1.34	1.56	1.17	1.36	3.94	2.90	1.22	2.66	2.19	3.33	10.20	3.07	0.32	1.19	3.75	1.46	3.27	2.24	7.41	18.79	2.54
100	1.60	2.40	1.49	1.73	2.55	1.48	1.87	6.26	3.35	1.70	3.37	1.98	4.49	15.97	3.48	0.50	1.72	3.43	2.66	5.96	2.24	10.02	30.48	3.04
	Average		1.55			1.53			2.66			2.22			4.47			3.52			2.51			3.32
	SD		0.27			0.58			0.83			0.51			2.75			1.95			0.89			1.64
	RSD		17.2			37.9			31.0			23.0			61.4			63.5			35.6			49.3

PAHs concentrations are expressed in ng/m^3 .

R: ratio between concentration obtained by Soxhlet extraction to water extraction.

(Spectrum Chemical Fact Sheet, 2001). On the other hand, the concentrations for the higher molecular weight PAHs (e.g. benzo[*a*]anthracene, chrysene, benzo[*b*]fluoranthene, benzo[*k*]fluoranthene, benzo[*a*]pyrene, Indeno[1,2,3-*c*, *d*]pyrene, Dibenzo[*a,h*]anthracene and Benzo[*g,h,i*]perylene using water were significantly lower than those reported for the Soxhlet method (ratio between 1.6 and 4.5). The lower concentrations of these compounds extracted by the present approach could be the result of either lower extraction efficiency, due to high non-polarity of these compounds or because the higher molecular weight PAHs are more tightly bound to the matrix active sites on the air particulate filter than soils or other matrixes.

4. Conclusions

In the present work, the optimization of variables associated with the extraction of PAHs in suspended particulate matter samples by using a subcritical water extraction system has been carried out. When a critical comparison is established between the proposed subcritical water extraction and the conventional Soxhlet extraction method, it can be concluded that, the time of analysis of sample preparation is decreased from 24 to <1 h. Furthermore, the organic solvent used in the extraction procedure can be decreased to <5%.

The method was applied to real samples of particulate matter in PM10 filters collected in downtown Santiago. The results provided by the proposed method agree satisfactorily with those obtained by the conventional Soxhlet method for low molecular weight PAHs and they are in agreement with concentration levels obtained for the Santiago metropolitan area determined by Didyk et al. (2000). Possible explanations for lower efficiency in the case of high molecular weight PAHs can be that the similar trend described previously (decreasing water solubility for higher molecular weight PAHs at ambient conditions) is observed for individual PAHs extracted under subcritical conditions. Another possible reason of this effect can be explained by the fact that higher molecular weight PAHs are more tightly bound to matrix active sites on the air particulate filter than soils or other matrixes.

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