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Rapid determination of inorganic elements in airborne particulate matter by using acidified subcritical-water extraction and inductively-coupled plasma–optical-emission spectrometry

Abstract A rapid and simple method has been developed for determination of inorganic elements in airborne particulate matter (PM10) by using acidified subcritical water and ICP–OES. Elements such as Al, As, B, Ba, Cd, Cu, Fe, Mn, Pb, Se, and Zn were rapidly and efficiently extracted from PM10 samples with a solution of 0.1 mol L^{-1} HNO_3 under subcritical conditions. The method requires approximately 5% of the amount of acid used in the standard microwave extraction procedure. The material selected for the subcritical extraction manifold was poly ether ether ketone (PEEK), to avoid sample contamination with elements present in previously reported stainless-steel manifolds. The extraction temperature, time of static and dynamic extraction, and flow rate of acidified water were studied keeping the pressure controlled at about 1,500 psig. The efficiency of extraction of most of the analytes increased with temperature, tending to quantitative extraction at temperatures near 150°C. After the extraction process the analytes were determined directly in the extract by ICP–OES. When the method was compared with the USEPA counterpart, the results indicate that under optimized conditions (static extraction time: 15 min, dynamic extraction time: 30 min, flow rate: 2 mL min^{-1}) the analytes were extracted with recoveries between 73 and 158%. Alternatively, by using an extraction time of 15 min, the method could be used to screen for all the elements, with recoveries over 50%. The developed method was applied to the determination of inorganic elements in airborne particulate matter in the atmosphere of Santiago, Chile.

Keywords Inorganic elements · PM10 samples · Acidified subcritical-water extraction · ICP–OES

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Introduction

One of the main problems associated with atmospheric contamination in Santiago, Chile, is airborne particulate matter (PM10). Evidence that this breathable material contains a series of organic and inorganic species that can affect the health of people makes its chemical characterization necessary.

Conventional sample-preparation techniques used for leaching of pollutants from solid matrixes are not only relatively slow but also aggressive to the environment, because they require large amounts of organic solvents or acids, depending on the nature of the analytes. In this context, nowadays the development of efficient, rapid and environmentally acceptable alternatives for sample preparation techniques is imperative [1–10]. It is important to point out that when recoveries must be quantitative, especially for complex samples, until now there has been no alternative to the use of procedures that are more aggressive. For analysis of simple materials or for rapid screening purposes, however, shortcuts can be viable.

The changes that occur in the physico-chemical properties of water, at high temperatures and pressures, have been recently exploited analytically in the extraction of low-polarity organic compounds from solid samples [5–10]. In this way, the decrease in the dielectric constant of water, together with the fact that faster diffusion, lower viscosity, and lower surface tension are achieved under this condition, enables the rapid extraction of low polarity organic compounds from the matrix. In this work the analytes of interest correspond to elements associated with an airborne particulate matter matrix. Considering this circumstance, subcritical water was acidified to make the attack on analyte–matrix interactions more efficient.

In this study the efficiency of acidified subcritical water (0.1 mol L^{-1} HNO_3) as an extraction fluid has been checked for the elements Al, As, B, Ba, Cd, Cu, Fe, Mn, Pb, Se, and Zn in PM10 samples. The method

under study was applied to the determination of elements in suspended particulate matter in the atmosphere of Santiago city.

Experimental

Reagents

All chemicals used were of analytical-reagent grade. Deionized water (Nanopure ultrapure water system; Barnstead, Dubuque, Iowa, USA) was used throughout. Subcritical nitric acid (Merck) solution (0.1 mol L^{-1}) was used for the extraction. The standard solution of elements was obtained from High Purity Standards (QCS-26).

Instruments and Apparatus

A schematic diagram of the extraction unit is shown in Fig. 1. All tubes (1/16″, O.D.) were made of poly ether ether ketone (PEEK). A Swagelok SS-ORS2 needle valve (5,000 psig allowed pressure) valve was employed. Stainless-steel components of the manifold used in previous studies [8, 9] for extraction of organic analytes could not be used in this study, because in the leaching process the steel was oxidized to some extent, even when pure subcritical water was used, giving rise to contamination of the extract with trace elements. In this situation the material selected for the manifold was PEEK, the same as is used for analysis by ion chromatography. Fernández-Pérez et al. [7] reported the use of subcritical water acidified with 4% (v/v) for trace metal leaching from coal samples. These authors report the presence of undesirable products as a result of leaching from the stainless-steel material used.

The extraction chamber consisted of a laboratory-made oven [8, 9] (a 28×12×5 cm temperature-controlled aluminium block). A BTC-704-41521000 temperature controler; Spec.: J, 0–400°C, was used to keep the temperature at the desired value. A preheated coil (2 m PEEK tubing, 0.030″ I.D., 1/16″ O.D., Dionex) was placed inside the chamber to maintain it at the programmed temperature, followed by the extraction cell
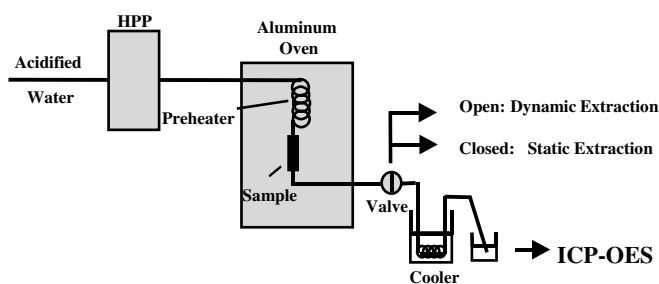

Fig. 1 Manifold used for acidified subcritical-water extraction of PM10 samples. *HPP*, high-pressure pump

(a 10 mm I.D. empty PEEK HPLC column, Dionex). The 0.1 mol L^{-1} nitric acid extracting solution was pumped using a HPLC pump (Waters model 600 pump) operated in the constant-pressure mode. For extraction, the working range of pressure inside the system was kept between 1,000 and 2,000 psig. After the extraction process the analytes were determined directly by ICP–OES (Perkin–Elmer, Optima 3300 XL). Extracts were also evaluated by ICP–MS (Fisons VG-PlasmaQuad) and HG–AAS (Perkin Elmer 1100B) to assess the quality of arsenic determination.

General analytical procedure

Impacted high-volume PM10 filters were treated under clean-air conditions (laminar flow cabin) taking care to minimize contamination and sample loss. Six circular parts per filter, equivalent to an area of 9.2 cm^2, were cut by using a hole-puncher of 14 mm diameter and extracted according to the following procedures.

Acidified subcritical-water extraction

All six circular filter portions (9.2 cm^2) were carefully crumpled and loaded into an extraction cell located inside the aluminium chamber–oven extractor. The oven was coupled to a heating device located on the upper part of the chamber and electronically controlled by means of a thermocouple until it reached 150°C. A static extraction time of 15 min was applied. Acidified water was then pumped through the system to extract the analytes from the particulate matter at a flow rate of 2 mL min^{-1} for 15 or 30 min, depending on whether screening or quantitative analysis, respectively, was being performed. After the acidified subcritical-water extraction the elements present in the liquid phase were determined by ICP–OES. The extraction was optimized by adjustment of the extraction temperature, static and dynamic extraction time, and flow rate of acidified water.

Conventional microwave extraction

The six circular filter portions (9.2 cm^2) were digested by using a Millestone MLS-1200 Mega plus EM-45 microwave oven and following USEPA Method IO-3.1 [11]. Basically, this consists of extraction of the elements using 10 mL hydrochloric acid–nitric acid solution.

Samples

Samples collected near the Caletones smelter (VI Region, Chile) were used for optimization purposes. In order to compare the performance of the method under optimized conditions, the results were compared with those obtained by microwave extraction [11]. PM10 samples collected at Cerrillos monitoring station

Table 1 Effect of the nature and concentration of the acid on extraction

Element	Relative signal[a]						
	HNO_3 (0.1 mol L^{-1})	HCl (0.1 mol L^{-1})	H_2SO_4 (0.1 mol L^{-1})	HNO_3 (0.1 mol L^{-1})	HNO_3 (10^{-2} mol L^{-1})	HNO_3 (10^{-2} mol L^{-1})	Pure water
As	1.00	0.70	0.46	1.00	0.74	0.61	0.25
Cu	1.00	0.74	0.56	1.00	0.70	0.24	0.14
Pb	1.00	0.35	0.41	1.00	0.70	0.32	0.16

[a]Signals were normalized to the highest response

(Metropolitan Region of Chile) were used to assess the application of the acidified subcritical-water extraction method under study.

Results and discussion

Study of variables

All the variables involved in the extraction process were studied by the univariate method. Impacted PM10 glass fiber filters, obtained from a monitoring station located near the Caletones smelter (VI Region, Chile), were used for optimization studies.

Effect of the nature and concentration of the acid

In order to assess the effect of nature of the acid and its concentration on the efficiency of the leaching process under subcritical conditions, hydrochloric, nitric, and sulfuric acids at 0.1 mol L^{-1} were assayed. Nitric acid was also studied at 0.01 and 0.001 mol L^{-1}. As can be seen in Table 1, for three representative elements (As, Cu, Pb), the extraction capability increases, for a fixed extraction time, in the order pure water < H_2SO_4 < HCl < HNO_3. Probably, the higher oxidizing capability of nitric acid aids the release of the elements from the particulate matter matrix and also favors the dissolution of the elements present as metal oxides. The best recoveries were obtained with 0.1 mol L^{-1} HNO_3. Decreasing the concentration of nitric acid decreases the recovery concomitantly. Higher concentrations of nitric acid up to 1 mol L^{-1} were assessed but recovery was not significantly improved.

Effect of extraction temperature

It is well known that airborne particulate matter is of two different kinds; primary particles come directly from emission sources and secondary particles are formed by reaction of primary pollutants in the atmosphere. Consequently, airborne particles comprise insoluble minerals, carbonaceous matter, ammonium sulfate, ammonium nitrate, chloride, K, Na, Ca, Mg, and trace metals associated with the matrix. The secondary inorganic components, sulfate, nitrate and ammonium, together with primary sodium chloride, are highly water-soluble. On the other hand, carbonaceous combustion particles and soil-derived minerals are relatively insoluble. Primary organic carbon is of low solubility but the more oxidized secondary organic component is substantially water-soluble. Some compounds of transition metals are highly water-soluble (e.g., nitrates and chlorides in general), whilst others such as oxides and sulfides, are typically less so. Taking these facts into account, it is highly probable that the solubility of each element differs depending on the nature of the bond with the matrix.

In this context, the effect of the acidified water temperature on element extraction was studied in the range 25–150°C. As can be seen in Table 2 for aluminium, copper, iron, barium, boron, and manganese, extraction efficiency was highly dependent on temperature, the best efficiency being clearly achieved at 150°C.

According to our results the elements aluminium, copper, iron, barium, boron, and manganese are probably strongly associated with the matrix of particulate matter as relatively insoluble minerals [12–16], consequently an increase in temperature favors the interaction of acidified water with the matrix, releasing these elements to a greater extent. In contrast, for arsenic, selenium, lead, zinc, and cadmium (Table 2), the extraction efficiency is almost constant in the temperature range under study (25–150°C). This fact, together with recovery studies shown below, is indicative that this group of analytes are adsorbed but not specifically associated with the matrix of particulate matter [17, 18]. It is not easy to determine exactly what physical-chemical forms

Table 2 Effect of temperature on acidified subcritical-water extraction of elements from airborne particulate matter

Element	Concentration (ng m^{-3})			
	25°C	50°C	100°C	150°C
Al	322.6	359.3	396.6	490.2
Cu	133.2	140.3	184.7	250.9
Fe	380.3	434.6	476.7	860.5
Ba	7.4	8.0	8.6	12.3
B	12.3	19.4	23.3	29.1
Mn	8.5	11.1	12.8	17.0
As	181.6	193.0	195.1	195.3
Se	5.8	5.8	5.8	6.2
Pb	81.1	85.2	84.8	85.2
Zn	63.4	63.4	63.6	69.3
Cd	2.3	2.8	1.9	2.5

of these species are present in the matrix, but probably lead and zinc are present as nitrates, and arsenic and selenium as soluble oxyanions [17, 18].

In any case, the effect of temperature observed in the extraction of cadmium and selenium is not clear because the concentrations determined are very close to the detection limit of the method.

Unfortunately, higher temperatures could not be checked because of the thermal instability of the material used in the manifold. Previous investigations made by Fernández-Perez et al. [7, 10] reported the use of acidified subcritical water (HNO_3 4%) for continuous extraction of arsenic, selenium, and mercury and arsenic, aluminium, and magnesium from coal. They established in both studies that the optimum temperature for extraction of these elements from coal was 180°C. In this context, while 150°C was employed the optimum value will be matrix and analyte-dependent.

Figure 2 shows the effect of static (stopped flow) time on extraction efficiency, for copper as a representative analyte. All elements show a similar behavior with this variable. As can be seen, static time has no significant effect on extraction because when static time increases, extraction efficiency increases only slightly. However, the application of static time was imperative for the precision of the method. The relative standard deviations (RSD, $n = 3$) of the response for static times of 0–5, 5–10, and 10–15 min, were 19, 14, and 5%, respectively. Hence a static time of 15 min was selected for further studies. In previous studies [8, 9], we have observed that this variable is not important for extraction of PAH and pesticides from solid matrixes. In this work on extraction of elements from PM10 filters it is necessary to consider the position and distribution of the sub-samples located in the extraction cell. The sub samples correspond to six impacted sections of the filter in which particulate matter is within the crumpled filter. For homogeneous acidified water penetration it is, therefore, imperative to apply a short period of static time.
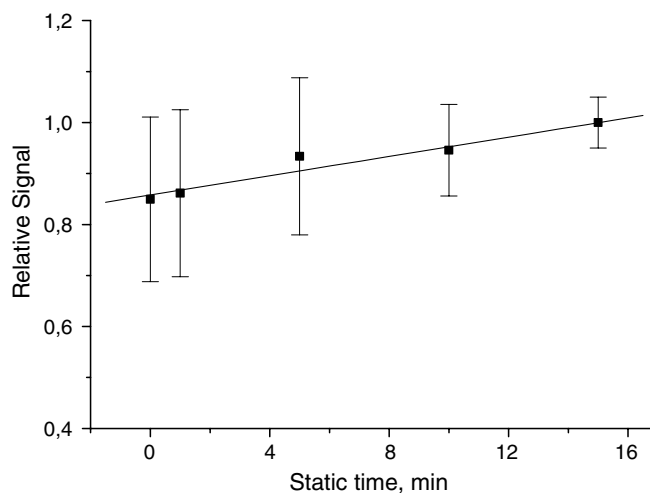

Fig. 2 Effect of static time on the acidified subcritical-water extraction of copper from PM10 filters

All previous variables were studied using a constant dynamic time of 30 min. It was observed that dynamic time is a very important variable, which favors the extraction process. In this context, when dynamic time was increased from 15 to 30 min, extraction efficiency increased an extent depending on the element (Table 3). A clear advantage of a dynamic extraction process over the batch static alternative such as conventional microwave extraction procedures is that, in the first case, the extraction solution is cooled outside the extraction cell, preventing the possibility of analyte re-adsorption on the solid matrix.

Effect of flow rate

The flow rate of acidified water was studied between 0.5 and 3 mL min^{-1}. No significant dependence of extraction efficiency on this variable was observed. However, a flow rate of 2 mL min^{-1} was selected because at this

Table 3 Analytical features of the method

Element	Reference value (ng m^{-3})[a]	Proposed method						Detection limit (ng m^{-3})
		Found (ng m^{-3})		Recovery (%)		RSD (%)[b]		
		15 min[c]	30 min[c]	15 min[c]	30 min[c]	15 min[c]	30 min[c]	
Al	683	439	499	64	73	8	10	32.4
As	161	200	194	125	121	2	2	13.9
B	33	25	29	78	89	30	29	24.9
Ba	13	11	13	86	98	17	20	4.3
Cd	2.1	1.6	2.1	75	100	8	14	1.1
Cu	258	234	262	91	101	8	8	6.7
Fe	933	727	857	78	92	14	13	9.2
Mn	19	17	17	90	89	4	2	1.9
Pb	73	86	84	117	114	4	3	3.7
Se	7.5	3.8	5.9	51	79	11	10	3
Zn	45	65	71	144	159	6	7	7.8

[a]Determined by following procedure established in Ref. [11]
[b]Relative standard deviation ($n = 3$)
[c]Dynamic extraction time

value better reproducibility was obtained. The relative standard deviations of the response for a flow rate of 2 mL min^{-1} were between two and three times lower than the observed for flow rates of 0.5 and 1 mL min^{-1}.

Validation and application of the method

Using the variables selected the method was applied to real samples of PM10 filters obtained from a monitoring station located in the VI Region, Chile, near a mining smelter facility. The method was compared with the USEPA standard method [11] which is based on microwave digestion. Table 3 shows the analytical features of the method for dynamic times of 15 and 30 min. According to these results a minimum of 30 min dynamic extraction is recommended for more quantitative purposes, because in this case the recovery was always over 73%, with quite acceptable precision. On the other hand, a 15 min extraction period is sufficient for screening purposes, considering a minimum recovery of 50%. The repeatability of the method depends mainly on static extraction time, as pointed out above. The high RSD observed for B, Cd, and Ba can be attributed to the proximity of the determined values to the detection limit of the method.

As can be seen in Table 3, if only determination of arsenic, zinc, and lead is required, 15 min is sufficient for quantitative extraction of the analytes. On the other hand, the considerably higher concentrations determined for these elements by the present method relative to the standard method, must be stressed. This might be not only because of more efficient extraction by acidified subcritical water but also because under the conditions established in the proposed method analyte loss by volatilization is lower than in the microwave digestion process, because in the proposed method the acid

evaporation step is not required. However, these high recoveries could also be because of contamination and spectral line interference.

The method was also applied to PM10 filters provided by the Metropolitan Environmental Health Service (SESMA) of Santiago, Chile, which were used in a research campaign [12] carried out in Santiago city between 1997 and 2000. The filters analyzed correspond to those used daily in the monitoring station located at Cerrillos (south–west of Santiago city) in July each year (winter time). One half of each filter sampled daily (24 h period) was analyzed by SESMA [19] by using microwave extraction and AAS for cadmium, manganese, zinc, copper, lead, and arsenic. The other halves were preserved and recently provided to us. In the present application we integrated a one-month sample by mixing in the extraction cell a whole circular area of 1.53 cm^2 of each filter. In this context, it is possible to compare our values with the monthly average determined by SESMA. As can be seen in Table 4, the same trends and orders of concentration, except for arsenic, are observed between the values. A more exact match between values is not feasible because of the different route followed to obtain them in both cases, as established above. However, in both cases it is possible to see a net diminution in concentration with time, which seems highly consistent with the implementation of the decontamination plan applied in Santiago since 1998. Particularly outstanding is the considerable attenuation of lead concentration due to the gradual elimination of leaded gasoline in Chile.

The difference between our arsenic values and those obtained by SESMA (Table 4), corresponding to one order of magnitude (10^{-2} compared with 10^{-3} µg m^{-3}, respectively), cannot be explained by differences in the extraction efficiency of the methods. As can be seen from Table 4, acidified water extracts obtained from independent portions of PM 10 samples collected in 1997

Table 4 Monthly average element concentrations in PM 10 samples collected at Cerrillos Monitoring station in the period 1997–2000 (month: July of each year)

Element	Proposed method (µg m^{-3})				SESMA method (µg m^{-3})			
	1997	1998	1999	2000	1997	1998	1999	2000
Cd	0.0035	0.0025	0.0030	0.0030	0.0025	0.0023	0.0030	0.0025
Mn	0.040	0.035	0.015	0.025	0.018	0.020	0.019	0.019
Zn	0.40	0.21	0.10	0.21	0.30	0.25	0.16	0.26
Cu	0.21	0.12	0.09	0.085	0.22	0.16	0.13	0.11
Pb	0.81	0.49	0.3	0.21	0.69	0.48	0.36	0.26
As	0.090	0.070	0.10	0.045	0.0078	0.0098	0.008	0.0057
	0.085[a]	–	–	0.035[a]				
	0.092[b]	–	–	0.047[b]				
Al	0.49	0.45	0.33	0.32	–	–	–	–
B	0.13	0.10	0.09	0.11	–	–	–	–
Ba	0.085	0.064	0.066	0.065	–	–	–	–
Fe	0.78	0.63	0.51	0.59	–	–	–	–
Se	0.0030	0.0023	0.0018	0.0020	–	–	–	–
PM10[c]	–	–	–	–	136	107	94	92

[a]Values determined by ICP–MS
[b]Values determined by HG–AAS
[c]Ref. [22] PM10 mean values in period 1st March–17th September

and 2000 were also evaluated for arsenic by ICP–MS and HG–AAS and in both cases the concentrations agree well with that determined by ICP–OES. On the other hand, by taking into account previous studies of arsenic concentrations in PM10 in Santiago, Chile, Artaxo [20] found in winter time 1998 average values for arsenic between 0.054 and 0.044 $\mu g\ m^{-3}$ at different monitoring stations in Santiago. On the other hand, Ulriksen and Cabello [21] established that the minimum average arsenic concentrations in PM10 in the Metropolitan Region of Chile are 0.02 $\mu g\ m^{-3}$, and in urban locations with industrial influence the concentrations are over 0.1 $\mu g\ m^{-3}$. Consequently, considering that Cerrillos monitoring station is located in a place with considerably high industrial activity, it is highly probable that the concentration values for arsenic given by SESMA were underestimated.

Other elements such as aluminium, boron, barium, iron, and selenium, which were not measured by SESMA, were also determined in the samples by the proposed method. As can be seen in Table 4, the average concentration of all this group of elements decreased in the period 1997–2000, which is mainly because the concentration of PM10 as a whole has been reduced in this period [22] (Table 4).

It is important to establish that the application of this analytical alternative in PM10 filters resulted in a appropriate screening method, which provides a similar level of information (presence of elements, good estimation of concentrations) compared with standard methods, but this level of information can be reached by using a significantly shorter analysis time.

Finally, apart from the efficiency of the proposed analytical alternative, it is important to state that routine use of this method not only reduces the cost of analyses, by saving time and acids, but also reduces environmental risks by minimizing acid wastes in the laboratory. Further, this approach also has a potential in remediation of contaminated soils or decontamination of solid wastes.

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