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ARTICLE

Combining Ultrasound-Assisted Extraction and ICP-MS for As, Cd, Cr, and Pb Determination in Atmospheric Particulate Matter

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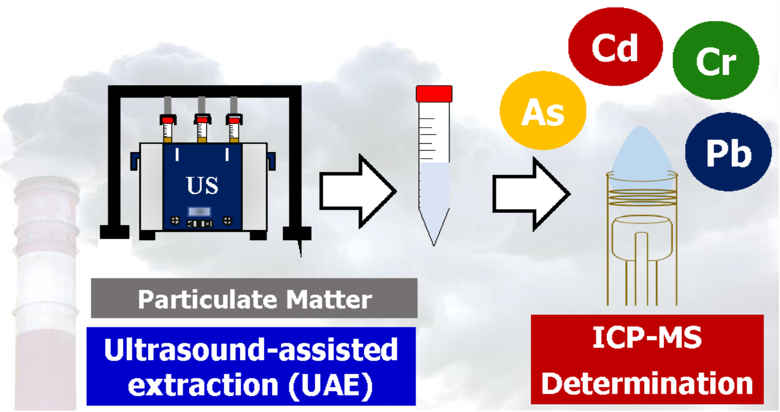

A simple, fast, and efficient ultrasound-assisted extraction (UAE) method for As, Cd, Cr, and Pb determination in atmospheric particulate matter (PM) by inductively coupled plasma mass spectrometry (ICP-MS) was developed. For the extraction procedure, the samples and the extraction solution were added directly into polypropylene vessels and placed in the ultrasound (US) bath. The following parameters were evaluated: *i*) sample mass: 50 to 500 mg, *ii*) extraction solutions: HNO_3, HCl, and HF, and *iii*) extraction time in the US bath: 10 to 30 min (80 °C). Accuracy was evaluated using certified reference materials (CRMs) of river sediment, (BCR 320, NIST 2704, and 8704) and by comparison with values obtained by using the method recommended by the United States Environmental Protection Agency (EPA 3052). The agreement with the CRMs and with the official method were better than 95% for all analytes when 100 mg of sample, 5 mL of an extraction solution containing 4.75 mL of 3:1 HNO_3:HCl (50%) + 0.25 mL of HF, and 20 min of heating (80 ºC) were used. Analytes were also determined by inductively coupled plasma optical emission spectrometry (ICP OES) and no statistical difference was observed (*t*-test, 95% confidence level) compared to ICP-MS results. The analyte concentration in the PM samples ranged from 6.60 ± 0.41 to 17.9 ± 0.9 $\mu g\ g^{-1}$ for As, from 0.839 ± 0.049 to 11.8 ± 0.6 $\mu g\ g^{-1}$ for Cd, from 31.3 ± 2.1 to 59.6 ± 3.5 $\mu g\ g^{-1}$ for Cr, and from 13.5 ± 0.5 to 123 ± 6 $\mu g\ g^{-1}$ for Pb. Low limits of detection (LODs) of 0.90, 0.015, 0.640, and 0.085 $\mu g\ g^{-1}$ were obtained for As, Cd, Cr, and Pb, respectively, which are important for the determination at low concentrations. Finally, the proposed method combined important advantages such as the use of a relatively low-cost sample preparation system (UAE method) with low reagent consumption, and a low volume of laboratory residues.

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INTRODUCTION

Air pollution has well-known harmful effects on humans, which can cause both acute and chronic diseases.[1-3] The emission of pollutants into the atmosphere and consequently their presence in street dust comes mainly from anthropogenic sources, such as industrial activities, waste incineration, urban construction, and motor vehicles, trucks, and motorcycles.[3, 4] In addition, natural sources, such as volcanoes, fires, and others can also contribute for the pollution.[4-7] Some data suggest that genetic damages can occur due to exposure to pollution and may increase the risk of cancer and other chronic diseases.[8-10] In this context, there is a growing interest in studying the toxic effects of air pollution, particularly atmospheric particulate matter (PM).[11-13]

Some pollutants, such as As, Cd, Cr, and Pb, which are potentially toxic to human health have been found in PM.[19-22] In this sense, the As, Cd, Cr, and Pb determination in PM is extremely important, even when present at low concentration.[23] However, despite the importance, the United States Environmental Protection Agency (EPA) only limits the presence to Pb in 0.15 µg m^3 in air.[16]

Analytical techniques, especially inductively coupled plasma mass spectrometry (ICP-MS)[24-26] and inductively coupled plasma optical emission spectrometry (ICP OES), which are highly sensitive, have been commonly used for the determination of As, Cd, Cr, and Pb in environmental samples.[27] However, it is necessary to apply a sample preparation method prior to the determination to obtain a suitable solution for analysis.[28-30]

The EPA recommends the official method 3052 for the digestion of PM samples for the subsequent As, Cd, Cr, and Pb determination by ICP-MS or ICP OES. In this method, the samples are digested in a microwave oven. However, the large amount of concentrated acids can increase the blank values and the limits of detection (LODs) and quantification (LOQs), as well as the laboratory residue generation. In addition, the high acid content in the final solutions obtained can lead to interferences in ICP-MS and ICP OES determinations.[31-33] Furthermore, sample digestion using the official EPA 3052 method requires a relatively high-cost microwave oven.

An alternative is the extraction methods, which can be considered simple and have been routinely employed for further metal and non-metal determination in organic and inorganic matrices.[34, 35] Additionally, ultrasound (US) can significantly improve the analyte extraction efficiency mainly due to the cavitation phenomenon effects, which is the process of bubble formation and their subsequent implosion.[36, 37]

In this way, an ultrasound-assisted extraction (UAE) method using diluted acid solutions for subsequent As, Cd, Cr, and Pb determination by ICP-MS in PM samples is proposed, for the first time. Operational parameters were evaluated: sample mass, extraction time, type and concentration of extraction solution. Samples used in this study were collected from air conditioner equipment in Chemistry Laboratories at the Federal University of Santa Maria (Santa Maria City, RS, Brazil). The accuracy was evaluated by the analysis of three certified reference materials (CRMs) of river sediment (BCR 320, NIST 2704, and NIST 8704) and by comparison with results obtained by using the official EPA 3052 method. Analyte determination was performed by ICP-MS. For comparison of results, the analytes were also determined by ICP OES. Finally, the UAE method was applied for the determination of As, Cd, Cr, and Pb in six PM samples.

MATERIALS AND METHODS

Instrumentation

Analyte determination by ICP-MS was performed using a spectrometer Model Elan DRC II (Perkin Elmer Sciex, Canada). For comparison of results, analytes were also determined using an ICP OES instrument Model Ciros CCD (Spectro Analytical Instruments, Germany). The experimental parameters used for the analyte determination by ICP-MS and ICP OES are selected as recommended by manufacturers.

The proposed UAE method was performed using a US bath system with a frequency of 37 kHz and a nominal US power of 200 W (Transsonic, Model TI-H-10, Elma, Germany). For comparison, a procedure at silent conditions (without the use of the US) was also performed. For this experiment, a hot plate with a magnetic stirrer (Polytron, Model PT 3100 D, Kinematica, Switzerland) was used. All extraction procedures were performed in polypropylene vessels (Sarstedt, Germany) with a conical bottom and a total volume of 15 mL.

For the comparison of the results, all the samples were digested as recommended by the EPA 3052 method.[38] For this procedure, a microwave oven (Multiwave 5000, Anton Paar, Austria) was used. This oven is equipped with a rotor of sixteen medium-pressure PTFE vessels (40 bar and 210 °C of maxima pressure and temperature, respectively).

Ash content was determined following the official ASTM D2974-14[39] method by applying the samples at 750 °C in a muffle furnace (Model LF0913, Jung, Brazil), for 2 h. The distribution of particle size was determined with a laser diffraction technique employing a particle size analyzer (Model Mastersizer 2000 Malvern, Germany). Before analysis, all samples used in this study were dried in an oven (Model 400/2ND, Nova Etica, Brazil), at 105 °C, for 2 h, and ground using a cryogenic mill (Spex Certi Prep, Model 6750, Metuchen, NJ, USA). After the extraction procedures, solutions were centrifuged (3450 rpm) for 5 min by using a centrifuge (Model Q22T208, Quimis, Brazil).

Reagents, solutions, and samples

Water used for the preparation of standards and reagents was previously purified (18.2 MΩ cm, Milli-Q system, Millipore, USA). Concentrated HNO_3 (65%, Merck, Germany) and HCl (37%, Merck, Germany) were previously purified by using a sub-boiling system (Model DuoPUR, Milestone, Italy). The concentrated HF (40%, Merck, Germany) was used without previous purification. Argon (99.998%, Air Products, Brazil) was used for both ICP OES and ICP-MS determinations.

Standard calibration solutions for the determination of As, Cd, Cr, and Pb by ICP-MS (ranged from 0.1 to 10 µg L^{-1}) and ICP OES (ranged from 10 to 100 µg L^{-1}) were prepared by dilution of the multielement stock standard solution (10 mg L^{-1}, SCP33MS, SCP Science, Canada) in HNO_3 (0.7 mol L^{-1}).

Six PM samples, named A to F, were used in this study. The PM samples were collected from air indoor filters located in laboratories at the Federal University of Santa Maria (city of Santa Maria, Rio Grande do Sul state, Brazil). All samples were collected on the same day and they were dried at 105 °C for 2 h, milled, and homogenized. The ash content in all samples was lower than 15% and particle size ranged from 10 to 25 µm. For accuracy evaluation, three CRMs of river sediment (BCR 320, NIST 2704, and NIST 8704) were used.

Reference EPA 3052 method

To obtain the reference values, the MAWD method in closed vessels was carried out as recommended by the EPA (3052 method).[38] In this sense, samples A and B (100 mg) were arbitrarily selected and they were digested by the MAWD method using a mixture of concentrated HNO_3 (4.5 mL), HCl (2.0 mL), and HF (1.5 mL) acids. The following heating program was applied: *(i)* 1200 W for 20 min and *(ii)* cooling step (0 W for 20 min). The temperature of each vessel was limited to 180 ± 5 °C. After cooling, the obtained solutions were diluted with water in volumetric flasks (up to 25 mL). The equipment of ICP-MS and ICP OES were employed for analyte determination. Before the determination step, a suitable dilution was applied to avoid damage by HF in glass parts of the ICP-MS and ICP OES equipment.

Proposed UAE method

For the proposed UAE method, samples were directly weighed into a polypropylene vessel (15 mL) and 5 mL of the extraction solution was added. Samples and extraction solution were mixed and submitted to the US bath (37 kHz, 60% of US amplitude, at 80 °C). The following parameters were evaluated: sample mass (50, 100, 250, and 500 mg), extraction time (10, 20, and 30 min), and type and concentration of extraction solution, as shown in Table I. After the extraction procedure, the final volume was completed to 10 mL and flasks were centrifuged for 5 min (3600 rpm). Finally, the As, Cd, Cr, and Pb determination were carried out by ICP-MS and ICP OES.

Table I. Evaluated solutions for As, Cd, Cr, and Pb extraction by UAE method

Evaluated extraction solution					
3:1 HCl:HNO_3	**3:1 HCl:HNO_3 + HF**	**3:1 HNO_3:HCl**	**3:1 HNO_3:HCl + HF**	**HNO_3**	**HNO_3 + HF**
100% (a)	50% (b) + 0.25 mL	50% (a)	50% (b) + 0.25 mL	100% (a)	50% (c) + 0.50 mL
50% (a)	25% (b) + 0.25 mL	25% (a)	25% (b) + 0.25 mL	50% (a)	35% (c)+ 0.50 mL
25% (a)	50% (c) + 0.50 mL				

(a) = 5 mL, (b) = 4.75 mL, (c) = 4.5 mL
Concentrated acids (65% HNO_3; 37% HCl; 40% HF)

An experiment in silent conditions (without the US) using mechanical stirring and conventional heating was also performed to compare results. This study applied the same optimized condition obtained by the UAE method. Finally, the As, Cd, Cr, and Pb determination were performed by ICP-MS and ICP OES.

RESULTS AND DISCUSSION

Proposed UAE method

The use of ultrasound using acidic solutions has been applied to many kinds of samples for further metal and non-metal determination.[40-43] However, a few studies have employed the UAE method for the determination of As, Cd, Cr, and Pb by plasma-based techniques in PM, especially for ICP-MS determination.

UAE method: extraction solution evaluation

The use of the US has demonstrated an increase in the extraction efficiency of analytes in comparison with conventional extraction methods, as reported in several works.[36, 43, 44] Thus, in this study experiments were performed to obtain suitable conditions for As, Cd, Cr, and Pb extraction in PM samples and subsequent analyte determination by ICP-MS.

Extraction solution evaluation experiments were carried out by using 100 mg of PM sample “A” and 5 mL of extraction solution, such as 3:1 HCl:HNO_3, 3:1 HNO_3:HCl (100, 50 and 25%), diluted HNO_3 solution with and without HF (0.25 or 0.5 mL). The acid solutions (as shown in Table I) were evaluated to obtain a suitable extraction condition for As, Cd, Cr, and Pb. Based on previous studies, operational conditions of the US system were kept at amplitude (60%), time (30 min), and temperature (80 °C).[45] Obtained results are shown in Figure 1 and they were expressed in agreement with reference results (obtained by the EPA 3052 method and analyte determination by ICP-MS).

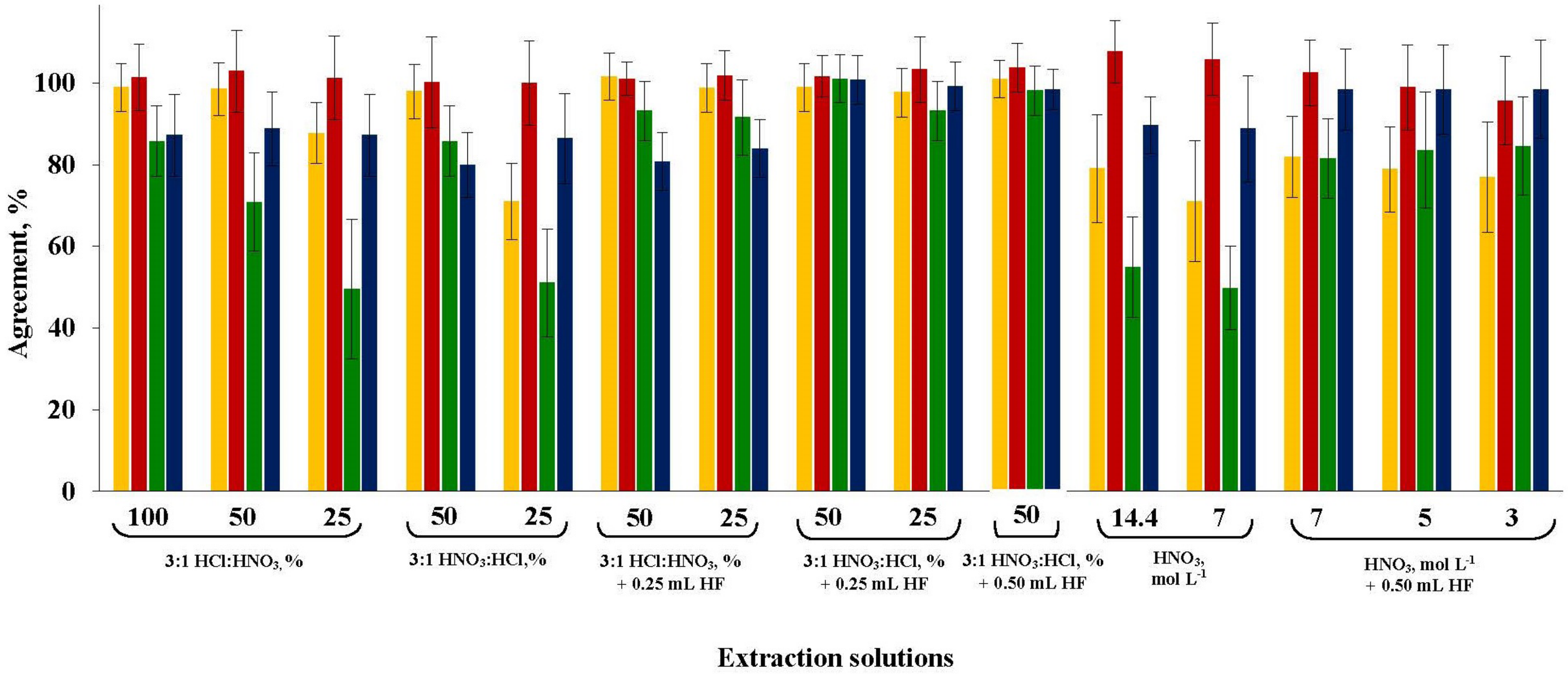

Figure 1. Results for (🟨) As, (🟥) Cd, (🟩) Cr, and (🟦) Pb on extraction solution evaluation by using the UAE method. Determination by ICP-MS. Experimental conditions: 100 mg of PM sample “A”, 5 mL of total extraction solution, 30 min of US, at 80 °C. Results as agreement with the official EPA 3052 method (mean and standard deviation, *n* = 3).

According to Figure 1, for As the use of 3:1 HCl:HNO_3 (100 or 50%) and 3:1 HNO_3:HCl (50%) were suitable for analyte extraction. However, for more diluted solutions of 3:1 HCl:HNO_3 or 3:1 HNO_3:HCl (both 25%), the obtained results were lower than 83% in comparison with the reference method. However, by adding HF to these solutions, results showed no statistical difference (*t*-test, 95% confidence level) compared with those obtained by the EPA 3052 method (as reference method). On the other hand, by employing only HNO_3 solution or HNO_3 + HF, unsuitable results were obtained (agreement were lower than 80%).

For Cd results, all the evaluated solutions agreed with the reference value (*t*-test, 95% confidence level). However, the relative standard deviations (RSDs) for conditions without the use of HF were higher (10%) than those using HF (5%).

For Cr, even using 3:1 HCl:HNO_3 (100, 50, and 25%), 3:1 HNO_3:HCl (50 and 25%) or HNO_3 (14 or 7 mol L^{-1} + HF) solutions, non-quantitative results were obtained (agreement lower than 50% in comparison with the reference results). On the other hand, by using the 3:1 HCl:HNO_3 + HF or 3:1 HNO_3:HCl + HF, better results were obtained for Cr. It is important to mention that using both solutions 3:1 HNO_3:HCl (50%) + 0.50 mL or 3:1 HNO_3:HCl (50%) + 0.25 mL of HF, results were in agreement with the reference method (*t*-test, 95% confidence level) and presented low RSDs (around 6%).

Similar results were obtained for Pb and suitable conditions were achieved by using 3:1 HNO_3:HCl (50%) + 0.25 or 0.50 mL of HF (same conditions previously described for Cr). Finally, it is important to consider that quantitative results were obtained for Cd e Pb by using diluted HNO_3 (7, 5, and 3 mol L^{-1}) solutions only when combined with HF (0.50 mL).

Even with the use in small volumes, HF reacts easily with the silicate present in the inorganic fraction and occurs the synergy with the effect of the ultrasonic energy applied in the medium, thus the analyte extraction occurs more easily to the solution.[46] On the other hand, the presence of HF can cause damage to the quartz surfaces of ICP-MS during the analyte determination. In this context, solutions using HF were diluted before analysis.[47]

According to the results shown in Figure 1, to obtain suitable conditions for all analytes, the use of HNO_3, HCl, and HF solutions was required. On the other hand, it is extensively discussed in the literature that the use of HCl (present in 3:1 HCl:HNO_3 and 3:1 HNO_3:HCl) can cause interferences on As determination by ICP-MS. During the determination of As by ICP-MS, the presence of $^{35}Cl^+$ (from HCl) and $^{40}Ar^+$ (from plasma) can result in polyatomic interference with the isotope of ^{75}As, resulting in non-quantitative results for this analyte.[48] In this sense, successive dilutions were performed before determining As by ICP-MS. Moreover, to verify the accuracy of the results, As was also determined by ICP OES. No statistical difference (*t*-test, 95% confidence level) was observed between the results by employing both techniques. In this sense, a suitable extraction solution containing 4.75 mL of 3:1 HNO_3:HCl (50%) + 0.25 mL of HF was recommended for the extraction of As, Cd, Cr, and Pb in PM samples and analyte determination by ICP-MS and ICP OES.

UAE method: sample mass evaluation

The amount of sample used in an extraction method is an important parameter to be evaluated and the use of high sample mass results in low LOD and LOQ, which are important to determine the analytes at low concentrations.[28] However, the high sample mass can contribute to obtaining non-quantitative analyte extraction due to the low contact surface between the sample and the extraction solution.[49] Thus, PM sample masses ranging from 50 to 500 mg were evaluated by employing the extraction solution, previously optimized 4.75 mL of 3:1 HNO_3:HCl (50%) + 0.25 mL of HF. The obtained results are shown in Figure 2.

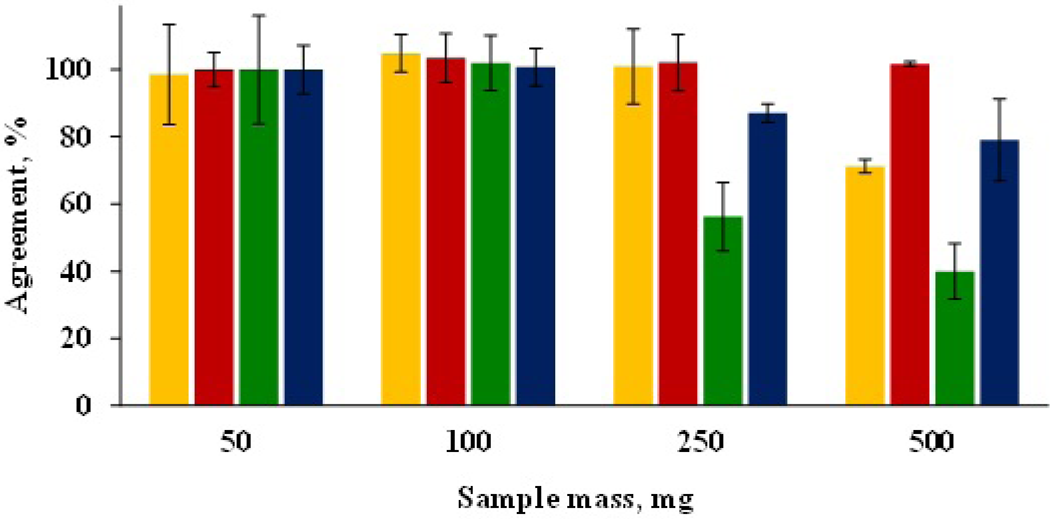

Figure 2. Results for (🟨) As, (🟥) Cd, (🟩) Cr, and (🟦) Pb for sample mass evaluation by using the UAE method. Determination by ICP-MS. Experimental conditions: PM sample "A" (50 to 500 mg), 4.75 mL of 3:1 HNO_3:HCl (50%) + 0.25 mL of HF as extraction solution, 30 min of US, at 80 °C. Results as agreement with the official EPA 3052 method (mean and standard deviation, *n* = 3).

According to all results shown in Figure 2, for Cr and Pb when 250 mg of sample were used, results were lower than reference values, agreement of 60 and 80%, respectively. In addition, for 500 mg of sample, the results for As, Cr, and Pb were also lower than reference values, agreement of 70, 40, and 75%, respectively. On the other hand, no statistical difference (*t*-test, 95% confidence level) was observed in comparison with reference results for all analytes when 50 or 100 mg of sample were employed, but the RSDs decreased when sample mass submitted to analysis was increased, as already reported in the literature.[49] In this sense, to achieve better LOQ, 100 mg of sample was selected as the maximum PM sample mass. In addition, the same condition was applied also for PM sample "B" and no statistical difference was observed when compared with reference results.

UAE method: extraction time evaluation

It is known that the time that a sample is exposed to the extraction is another important parameter to be optimized. In the present study, the efficiency of extraction was evaluated by applying 10, 20, and 30 min of US, 60% of amplitude, 80 °C, 100 mg of PM sample "A", and 5 mL of the extraction solution previously optimized (4.5 mL of 3:1 HNO_3:HCl (50%) + 0.25 mL of HF).

For comparison of results, a silent extraction procedure was also carried out using mechanical stirring (2000 rpm), without US application. This comparison was carried out using 10, 20, and 30 min of extraction time at 80 °C, 100 mg of PM sample "A", and 5 mL of the extraction solution (4.75 mL of 3:1 HNO_3:HCl (50%) + 0.25 mL of HF). The As, Cd, Cr, and Pb determination were performed by ICP-MS. The results for all evaluations are shown in Figure 3.

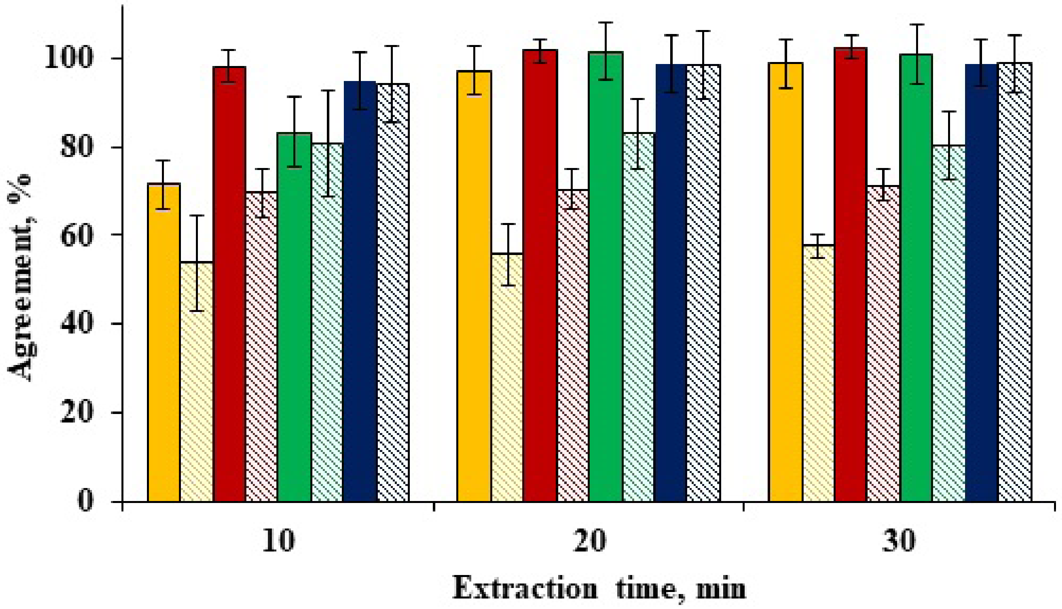

Figure 3. Results for (🟧) As, (🟥) Cd, (🟩) Cr, and (🟦) Pb after ultrasound and (▨) As, (▨) Cd, (▨) Cr, and (▨) Pb after mechanical stirrer on extraction time evaluation (10 to 30 min). Experimental conditions: 100 mg of PM sample "A", 4.75 mL of 3:1 HNO_3:HCl (50%) + 0.25 mL of HF, at 80 °C. Determination by ICP-MS. Results as agreement with the official EPA 3052 method (mean and standard deviation, *n* = 3).

As shown in Figure 3, for Pb by employing the US or mechanical stirrer, results were in agreement with reference values for all evaluations (10, 20, or 30 min). Similar results were obtained for Cd, which were in agreement with reference values, independent of US time applied. However, for all experiments using a mechanical stirrer, results for Cd were lower than 70% in comparison with reference values.

For As and Cr, quantitative results were obtained only when the US was applied for 20 or 30 min. In this sense, 20 min of US was chosen as a suitable condition for the UAE method for the extraction of As, Cd, Cr, and Pb in PM samples and subsequent analyte determination by ICP-MS.

Accuracy evaluation

The accuracy of the UAE method was evaluated by employing river sediment CRMs (BCR 320, NIST 2704, and NIST 8704). Extractions were performed applying the optimized conditions of 4.75 mL of 3:1 HNO_3:HCl (50%) + 0.25 mL of HF, 100 mg sample, 20 min of US extraction (60% of US amplitude), at 80 °C.

Moreover, for the accuracy evaluation, all PM samples were digested as recommended by the EPA 3052 method for subsequent As, Cd, Cr, and Pb determination. This method recommends the sample digestion by MAWD using a mixture of concentrated acids in a closed system. A mixture containing HNO_3, HCl, and HF (total volume of 8 mL) was used for the complete digestion of samples with high silica content.[16] Analyte determinations were performed by ICP-MS. The results are presented in Table II.

Table II. Results for As, Cd, Cr, and Pb in CRMs of river sediment and samples of PM by ICP-MS after the UAE and MAWD methods. Mean and standard deviation are expressed in µg g^{-1}, *n* = 3.

PM Samples µg g^{-1}	**As**		**Cd**		**Cr**		**Pb**	
	UAE	**MAWD**	**UAE**	**MAWD**	**UAE**	**MAWD**	**UAE**	**MAWD**
A	8.51 ± 0.59	8.60 ± 0.81	4.99 ± 0.36	4.83 ± 0.31	59.6 ± 3.5	59.0 ± 5.2	123 ± 6	125 ± 11
B	10.6 ± 0.7	10.2 ± 0.6	11.8 ± 0.6	11.2 ± 0.5	31.3 ± 2.1	33.3 ± 2.1	86.2 ± 6.1	81.3 ± 6.7
C	11.7 ± 0.8	11.0 ± 0.7	2.23 ± 0.09	2.33 ± 0.14	38.3 ± 2.5	41.1 ± 3.3	102 ± 3	109 ± 5
D	12.1 ± 0.7	11.8 ± 1.1	0.999 ± 0.049	1.08 ± 0.06	36.2 ± 1.4	38.4 ± 2.1	60.9 ± 2.0	64.5 ± 1.3
E	6.60 ± 0.41	6.05 ± 0.56	0.839 ± 0.049	0.788 ± 0.053	49.3 ± 2.1	50.6 ± 2.2	13.5 ± 0.5	14.3 ± 0.9
F	17.9 ± 0.9	16.5 ± 1.5	2.99 ± 0.25	2.89 ± 0.17	33.2 ± 2.4	35.9 ± 2.5	86.9 ± 7.8	90.4 ± 4.1
A*	8.77 ± 0.67		4.73 ± 0.41		62.9 ± 3.9		116 ± 8	
	Certified value	**Found value**	**Certified value**	**Found value**	**Certified value**	**Found value**	**Certified value**	**Found value**
NIST 2704	23.4 ± 0.8	22.8 ± 0.3	3.45 ± 0.22	3.26 ± 0.11	135 ± 5	135 ± 10	161 ± 17	150 ± 7
NIST 8704	17.0	17.7 ± 0.9	2.94 ± 0.29	2.90 ± 0.13	122 ± 4	125 ± 9	150 ± 17	153 ± 9
BCR 320	76.7 ± 3.4	80.4 ± 3.3	0.533 ± 0.026	0.563 ± 0.023	138 ± 7	131 ± 9	42.3 ± 1.6	41.3 ± 2.1

Sample A*: results were obtained by ICP OES for accuracy evaluation.

According to the data shown in Table II, results for As, Cd, Cr, and Pb in all CRMs evaluated using the UAE method presented no statistical difference with the certified values (for all analytes, the RSDs were lower than 10%). In addition, no statistical difference was found in comparison with values obtained using the reference method (EPA 3052 method). As an additional experiment, As, Cd, Cr, and Pb were also determined by ICP OES and results were compared with those obtained by ICP-MS. The results are shown in Table II. No statistical difference (*t*-test, 95% confidence level) was observed for all analytes and samples investigated (except for Cd in samples D and E where the concentration was lower than LOD).

It is important to consider that analyte concentration in PM samples ranged from 6.60 ± 0.41 to 17.9 ± 0.9 µg g^{-1} for As, 0.839 ± 0.049 to 11.8 ± 0.6 µg g^{-1} for Cd, 31.3 ± 2.1 to 59.6 ± 3.5 µg g^{-1} for Cr, and 13.5 ± 0.5 to 123 ± 6 µg g^{-1} for Pb (determination by ICP-MS). Furthermore, these results showed that the toxic elements concentration in the PM samples collected from air indoor filters was relatively high and in a wide range. It can be considered a problem since these elements even at low concentrations can lead to several problems to human health when they are inhaled or ingested.

CONCLUSION

The proposed UAE method using a diluted solution of HNO_3 and HCl associated with a few microliters of HF was proven to be a feasible sample preparation method for PM samples and further As, Cd, Cr, and Pb determination by ICP-MS. Using the extraction method, it was possible to use sample masses of up to 100 mg with only 5 mL of a solution of 4.75 mL of 3:1 HNO_3:HCl (50%) + 0.25 mL of HF, 20 min of extraction (60% of US amplitude), at 80 ºC. The accuracy was evaluated by applying a CRM of river sediments and also by comparison with those results obtained after EPA (determination by ICP-MS). The LODs obtained for As, Cd, Cr, and Pb were as low as 0.90, 0.015, 0.640, and 0.085 µg g^{-1}, respectively. A clear advantage of the proposed method can be related to the reduction of the high volume of reagents required for sample digestion, which represents a significant decrease in residue generation. It is important to consider that these aspects are in agreement with the green chemistry recommendations. In summary, the proposed UAE method can be simple, because the instrumentation for sample preparation is easy to use and accessible in many laboratories, rapid, and highly sensitive for subsequent simultaneous extraction of As, Cd, Cr, and Pb and further determination by ICP-MS.

Conflicts of interest

The authors have declared no financial conflicts of interest. This includes all potential sources such as affiliations, funding sources and financial or management relationships which may constitute a conflict of interest. Moreover, they declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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