INTERNATIONAL JOURNAL OF ENVIRONMENTAL ANALYTICAL CHEMISTRY, Vol. 86, Issue 9, on 2006

available at: https://doi.org/10.1080/03067310600584020

Chemical speciation of trace metals in fine airborne particles: advances in operational performance of a new sequential extraction scheme

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Abstract. A speciation method of inorganic metal compounds in airborne particulate matter based on selective sequential extractions is described. The sequential leaching procedure was perfected for improvement of performance at different stages of scheme. The loss of fine particles during the leaching procedure was the main source of error that was assessed and corrected. Loss of sample volume due to the heating steps and due to the absorption on filter material was also a difficulty to solve. New experimental conditions were optimized for the operational scheme to remove the different sources of loss. Microwave assistance with an optimum programme as a heating system, filtration of extractable solutions, and the use of internal standards were the main contributions.

Keywords: Chemical speciation; Metals; Atmospheric particles; ICP-AES; Optimization

1. Introduction

Speciation of trace elements in environmental analysis is a recent topical issue that constitutes an answer to finding the effects of metals in the environment, implying a new viewpoint for analytical control [1]. Determination of chemical species in the air is an essential part of any study of pollution in this environmental compartment. Metal speciation in airborne particles is less well studied, owing to the difficulties encountered in obtaining the total concentrations in most types of atmospheric samples [2].

Determination of total metals in the air is well described in the literature. Methods for speciation on solid mixtures of metal species in atmospheric monitoring are also reported. Many other chemical procedures are described in the literature for metal speciation in solid matrices such as sludge, river and lakes sediments [3, 4], and

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contaminated land [5]: most of them based on the Tessier procedure [6] in which metals are divided into acid-soluble, exchangeable, reducible, and oxidable fractions.

A new sequential extraction procedure was optimized in 1996–1997 during a doctoral thesis [7]. The sequential scheme was fractionated into four stages (fraction): (1) soluble and exchangeable elements, (2) elements bound to carbonates and Fe/Mn oxides-reducible elements, (3) elements bound to organic matter-oxidable elements and sulphides, and finally (4) residual elements. The 1996–1997 optimization was focused on the development of a chemical speciation scheme specially applied to fine airborne particles in order to determine the chemical forms available to the human body through the respiratory tract. The purpose of the present optimization was to improve the previous scheme (table 1) tested in 1994–1995.

The procedure is described completely in Fernández-Espinosa *et al.* [10]. Briefly, it involved testing different experimental conditions on synthetic samples of particulate matter and then verified on real samples of fine particles. The concentration of reagents, pH, temperature, and extraction time values, were the optimized variables. The airborne particulate matter constituted a different matrix to the soil, sludge, or sediment matrices. Thus, the experimental parameters for analytical separations of chemical forms from particles were optimized.

Finally, the optimized final scheme of 1996–1997 (table 2) was applied to the study of the air pollution problem of Seville (Spain), a city of >700 000 which was influenced

Table 1. Previous scheme: Speciation scheme according to Obiols [8] and Fernández *et al.* [9].

Metallic fraction	Reagent	Experimental conditions
1. Soluble and exchangeable metals	25 mL of 1% NaCl	Mechanical agitation during 60 min at room temperature
2. Carbonates, oxides and reducible metals	25 mL of 0.04 M $NH_2OH \cdot HCl$ in 25% HAcO	1 h at 95 °C, agitating occasionally
3. Bound to organic matter, oxidisable and sulphidic metals	25 mL of 0.02 M HNO_3 + 10 mL 30% H_2O_2 + 3 mL 30% H_2O_2 + 5 mL of 3.2 M NH_4AcO in 20% HNO_3	90 min at 85 °C, 1 h at 85 °C, continuous agitation 30 min at room temperature
4. Residual metals	5 mL of conc. HNO_3 + 2 mL of conc. HCl + 20 mL H_2O	90 min at 95 °C, agitating occasionally

Table 2. Proposed scheme: Speciation scheme according to Fernández [7] (the sequential extraction procedure was optimized in 1997 [10]).

Metallic fraction	Reagent	Experimental conditions
1. Soluble and exchangeable metals	15 mL H_2O (pH = 7.4)	3 h at room temperature; shaker agitation
2. Carbonates, oxides and reducible metals	10 mL $NH_2OH \cdot HCl$ 0.25 M at pH = 2.0	5 h at room temperature; shaker agitation
3. Bound to organic matter, oxidizable and sulphidic metals	7.5 mL H_2O_2 30% + 7.5 mL H_2O_2 30% + 15 mL NH_4AcO 2.5 M, at pH = 3.0	At 95 °C until near dryness; shaker agitation + at 95 °C until near dryness; shaker agitation + 90 min at room temperature; shaker agitation
4. Residual metals	10 mL ($HNO_3 : HCl : HClO_4$) (6 : 2 : 5)	5 h at 95 °C; shaker agitation

mainly by traffic, but also by resuspended land and some important industries. When experimental conditions of both 1994–1995 and 1996–1997 schemes were applied to the same samples, profiles of chemical form concentrations were different in many metals (figure 1). These changes were attributed to the employment of less aggressive conditions in the new scheme of 1996–1997. The optimization of this new scheme was satisfactory and, applied to the study of air pollution in Seville, showed agreement with the expected results.

However, performance of the complete scheme is quite arduous and entails careful handling during the long execution period. In addition, several operational problems, such as the efficiency of physical separation between the solid phase

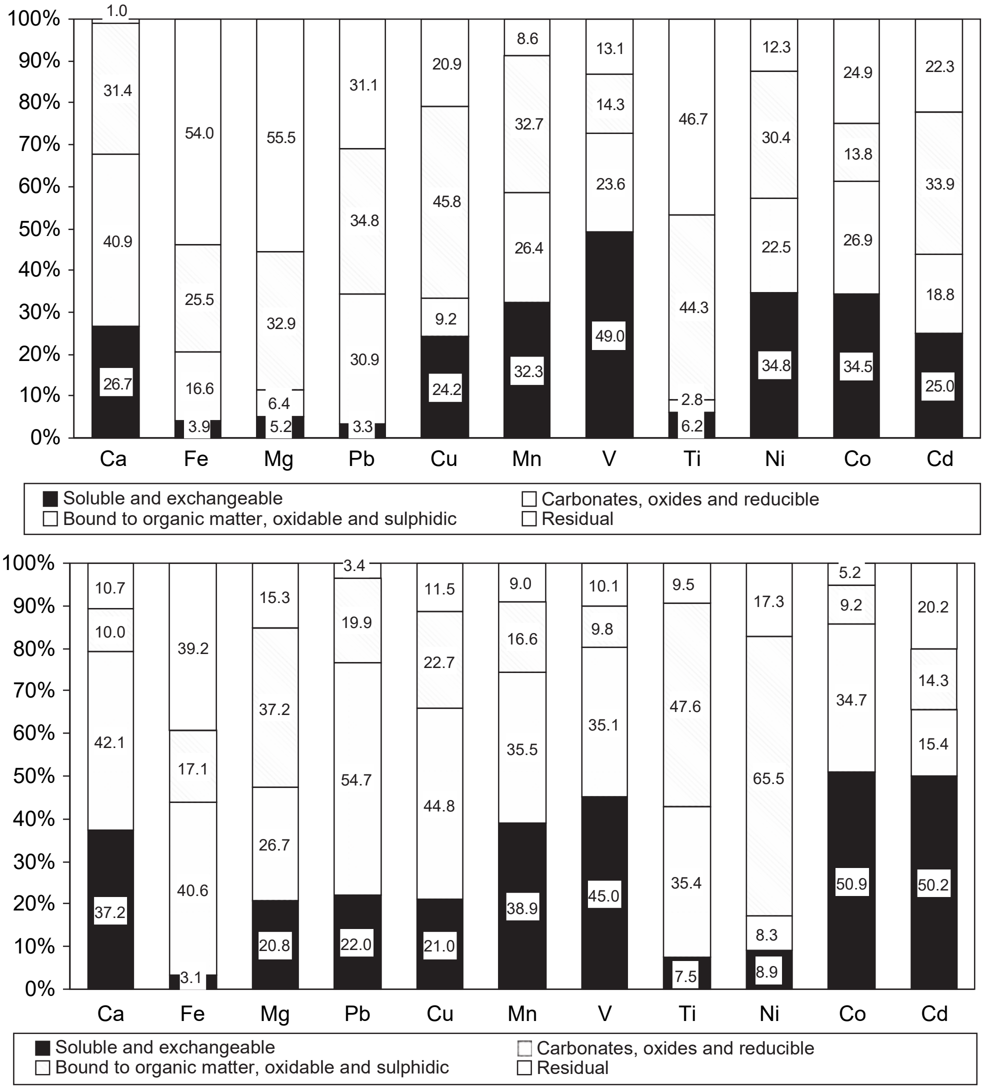

Figure 1. Change in the speciation profiles of the 11 metals. (*a*) Speciation scheme according to Fernańdez-Espinosa [7]; (*b*) Speciation scheme according to Obiols et al. [8].

(particles plus filter) and the liquid phase (aqueous extract), hinder the complete scheme. New technologies allow the best performance of analytical methods. Chemical speciation methods constitute complex analyses, which require improvements and process of validation. The operational speciation schemes are a set of chemical and physical separations of chemical compounds in solid samples. Any new technique or experimental condition that improves the efficiency of these separations must be included in the method for its perfection. In order to facilitate performance and increase efficiency of physical separation, the scheme optimized in 1996–1997 was improved in 2003–2004. Consequently, the aim of the current work is to present the new improvements and advances of the final scheme.

2. Experimental

2.1 Sampling

Atmospheric particulate matter used for laboratory tests was collected with a high-volume sampling system (MCV, Model CAV-A/HF Barcelona, Spain) equipped with a five-stage standard cascade impactor (MCV, Model IC/CAV) with a backup filter. Sampling periods were 24 h. Quartz filters were purchased from WHATMAN (QM/A) (Middlesex, UK).

The impactor effectively separates the particulate matter into six stages, with the following equivalent cutoff diameters, at 50% efficiency: >10, 10–4.9, 4.9–2.7, 2.7–1.3, 1.3–0.6, and <0.6 mm (0.61–0.01) (Backup). In this current work, filters from stage 6 (backup) of the same sample set were divided into pieces of fourths, sixths, eighths, and twelfths to carry out the different tests to improve the chemical speciation scheme. Therefore, all speciation data refer to the fraction <0.6 mm a.e.d.

Twelve samples were collected to perform the different experimental tests. They were selected from a set of samples collected under similar meteorological conditions: on the same day of the week and at the same location. After sampling, all filters were stored in darkness at room temperature and at a relative humidity of less than 5%. Care was taken in handling the quartz filters in order to avoid contamination problems, and all filter materials and samples were handled within a vertical laminar airflow cabinet, thereby ensuring air cleanliness standards of class 100 according to Federal Standard 209E [11].

2.2 Reagents and apparatus

The vertical laminar airflow cabinet was from Indelab (Navarra, Spain) with a HEPA filter (Model IDL-48V). The centrifuge was from Sigma (Osterode am Harz, Germany) (Model 3–15) with a rotor for eight centrifugal tubes of 50 mL of capacity. Nitric, hydrochloric and perchloric acids, hydroxylamine chloride, ammonium acetate and hydrogen peroxide, and standard solutions for metals were from Merck (Darmstadt, Germany). Milli-Q-grade water was from Waters-Millipore (Billerica, MA, USA) (Model Plus).

The water bath for heating was from Julabo (Seelbach, Germany) (Model SW-20C). The microwave oven was from Millestone (Seelbach, Germany) (model Ethos 900). The vertical rotator (50 rpm) for agitating centrifugal tubes during the leaching process was from Agitaser (Barcelona, Spain). The nylon filters (47 mm diameter, 0.22 μm porous) used for filtration of extractable solutions were from Teknokroma (Barcelona, Spain). The microbalance for weighing of Nylon filters was from Perkin-Elmer (Wellesley, MA, USA) (model AD-04 Autobalance). The balance for weighing the PTFE reactor of the microwave system was from Mettler (Küsnacht, Switzerland), model P2010. The reflectometer for determining the opacity of the nylon filters was from McLeod (Morgan Hill, CA, USA).

The sample extractions were analysed in four chemical fractions for 16 elements (Na, K, Ca, Mg, Al, Ti, V, Cr, Mn, Fe, Co, Ni, Cu, Zn, Pb, and Cd) by inductively coupled plasma atomic emission spectrometry (ICP-AES) using a Fisons-ARL (Accuris, Switzerland), 3410 sequential instrument.

3. Results and discussion

The chemical separation of metals was already optimized in 1996–1997. The different physical separations constituted the principal cause of efficiency loss in speciation methods. The efficiency of physical separation depends on several factors, which we studied previously. The main reason for poor recovery in physical separation is partial loss of the sample. The different causes that provoke this physical sample loss (loss of particles) were classified by our group into four factors: first, the loss of sample volume during heating; second, the loss of particles separated from the filters during leaching; third, the loss of particles during the pouring of solutions; and fourth, volume loss of sample during the washing effect of filter materials. These causes have constituted the structure of the different improvements. Finally, the acid mixture applied in the last fraction was adapted to the new heating system, the microwave.

3.1 Loss of sample during heating: microwave assistance

The previous schemes of 1996–1997 and 1994–1995 used a water bath as the heating system in fractions 3 and 4. Centrifugal tubes containing filters of particles and reagents were heated in the water bath. This heating system causes frequent accidental losses; for instance, closed tubes can deform, break, or explode in fraction 4 (acid digestion in the closed recipient). Also, the aqueous content can partially evaporate from an open tube, and metals can volatilize in fraction 3 (evaporation in open recipient). These accidents hinder the performance for the whole of the four fractions, the complete scheme.

Other heating techniques, such as the use of a microwave oven with hermetic PTFE vessels, offer better results. In addition, with a microwave oven, samples can be heated in a shorter period of time, and a high number of samples can be processed, so heating was carried out in a microwave system. In order to find the optimum power programme, various possibilities were tested.

Forty-eight pieces of four filters of particles were used during the optimization testing. The carousel of the microwave contains six PTFE vessels. The test for each filter was performed twice. In each test, two-twelfths of one of the filters were submitted to the different power programmes, and then duplicated. In each heating programme, two-twelfths of the filter were put into two PTFEs, one in each. The remaining four vessels were filled with only the corresponding reagents, without filter pieces. The six different programmes were tested in fraction 3 (destruction of organic matter) and in fraction 4 (acid digestion of the final residue). The weight of the PTFE vessels before and after heating and the total concentration of metals were the two variables evaluated to assess the possible loss of sample volume and loss of metal concentration. A gold internal standard was employed to evaluate the possible loss of metal concentration, knowing well that the gold element is not present in airborne particle samples. The different tests were applied to test the different programmes to filter particles after application of the procedure to extract the first two fractions of the speciation scheme, optimizing fraction 4 after fraction 3 was optimized. Filters were placed in closed PTFE vessels with the corresponding volume of reagent and heated according to the different programmes. After heating and cooling, sample solutions were transferred into conical sterile tubes.

The optimum power programme selected was the same for both fractions 3 and 4 (table 3). Programme P4, with a slight and continuous increase in power between stages, was selected because it produced the best results obtained for both fractions 3 and 4. No loss of volume sample and metal concentration was observed. In addition, in Fraction 4, residual particles became colourless, and filters were completely white as opposed to the water bath system.

3.2 Loss of particles during leaching: centrifugation programme

The loss of efficiency in the fractionation of metals is also caused by particles separated from filters during the leaching procedure. After the samplings, airborne particles are strongly integrated into the quartz filter structure. Before the beginning of the speciation scheme performance, a quarter of a filter was introduced into the centrifugal tube after it was cut into pieces of 1 cm^2 (approximately 100 pieces). However, in the leaching process of fractions 1 and 2, an appreciable portion of particles was separated from the filter inside the centrifugal tube due to the agitation of the vertical rotator. Thus, the atmospheric particles moved away from filters, passing to the extractable solution phase, and, consequently, to the flasks. To avoid this partial loss, an optimum programme of centrifugation was investigated and found.

The speciation scheme optimized in 1996–1997 involved centrifuging the samples at 5000 rpm for 10 min. Thus, different tests to combine an increase in speed and time

Table 3. Microwave programmes tested for fractions 3 and 4 of the chemical speciation scheme.

	Programme											
	P1		P2		P3		P4		P5		P6	
Stage	Time (min)	Power (W)	Time (min)	Power (W)	Time (min)	Power (W)	Time (min)	Power (W)	Time (min)	Power (W)	Time (min)	Power (W)
1	3	250	3	250	2	250	6	250	10	800	5	250
2	2	0	3	0	1	0	6	400	10	400	5	400
3	5	250	5	250	5	400	6	650	–	–	5	600
4	2	0	3	0	10	600	6	250	–	–	5	250
5	3	500	2	400	4	500	–	–	–	–	–	–
6	2	0	3	0	–	–	–	–	–	–	–	–
7	3	500	2	400	–	–	–	–	–	–	–	–

of centrifugation constituted the experimental design to find the optimum conditions. After each programme of centrifugation, the liquid was filtered with a vacuum filtration system and transferred to the conical sterile tubes. The lost particles were quantified by measuring two parameters: the weight of particles filtered and the opacity of these nylon filters by optical reflectometry. The different centrifugation programmes were applied to nine pieces of two different filters. The optimum programme found is shown in figure 2. The optimized final conditions were finally 7500 rpm for 15 min. In this way, pieces of filters were collected near the bottom of the tubes and there the particles were strongly embedded in the pieces of filters. Thus, loss of separated particles was minimized at below 1% of the total amount of particles lost.

3.3 Loss of particles during the pouring of solutions: filtration

In spite of an optimum centrifugation, a small quantity of fine particles (<1%) is lost when the extractable solution is decanted and transferred to the sterile tubes. Filtration or ultra-centrifugation could eliminate the loss of residual particles. The ultra-centrifugation technique requires the transfer of the whole filter plus liquid (metals extracted by the specific reagent) to another centrifugal tube, because the ultra-centrifuge uses a different type of tube. Any transfer of samples must be avoided in order to minimize any further loss. Filtration of the extractable solution maintains the residues (filters plus particles) in the same centrifugal tube without transferring them. Nevertheless, the filtration needed a design modification.

The filtration was done using an apparatus of filtration under a vacuum of small volume (100 mL). The sterile tube was placed in the sidearm flask, and the exit of

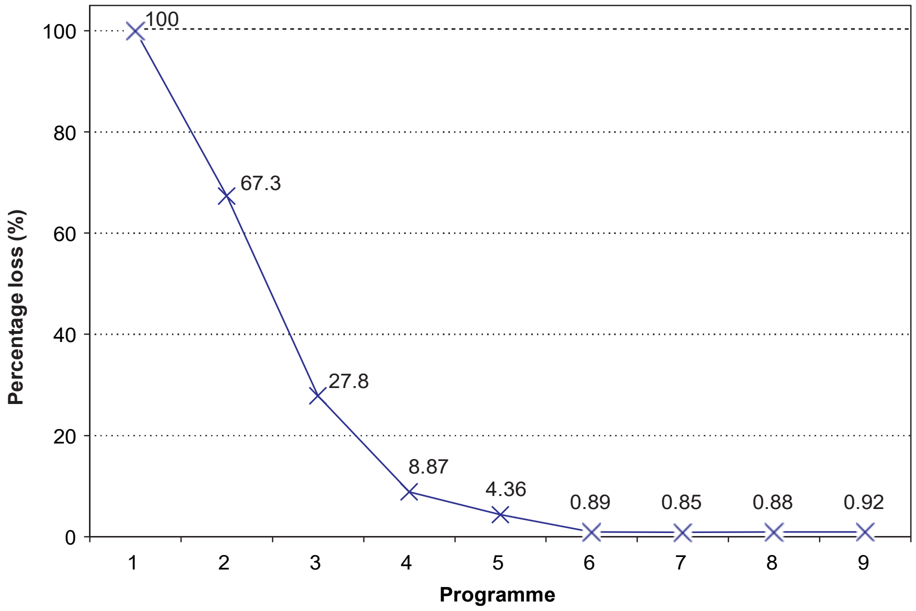

Figure 2. Optimization of the centrifugation stage. The percentage loss represents the ratio (mass of particles þ 1/R)$_{\text{program } i}$/(mass of particles þ1/R)$_{\text{program } 1}$ -100. Programmes: 1, 5000 rpm 3 min; 2, 5000 rpm 5 min; 3, 6000 rpm 5 min; 4, 6000 rpm 10 min; 5, 7000 rpm 10 min; 6, 7500 rpm 10 min; 7, 7500 rpm 15 min; 8, 8000 rpm 15 min; 9, 8000 rpm 20 min.

porous filter of the membrane filtration system was introduced into the top of the conical tube, as can be seen in figure 3, in order to avoid the loss or contamination of solutions due to the transfer from the suction flask. The design allows extract and residue transfer to be avoided. The dirty filter containing the lost particles was returned to the centrifugal tube, adding it to the residue. Two different filters loaded with different amounts of particles were cut into four equal pieces. These were used for testing by duplicating the designed filtration, which no loss of sample observed. Measurement of blanks that included the dirty nylon filters demonstrated that these filters introduced no contamination.

3.4 Loss of sample during the washing effect: internal standard

Quartz filters absorb an important portion of leaching solution when they are damp. Filters are dry when the speciation procedure begins in fraction 1 (addition of 22 mL of H_2O at pH 7.4), but after extraction, the residue of fraction 1 is wet, retaining 5–6 ml of the 'soluble and exchangeable' solution, which can pass to fraction 2. Washing of the residue with the same extractable solution (H_2O at pH 7.4) transfers part of the volume of solution occluded in the residue to the first solution extracted, diminishing the volume retained by cut filters. However, with the aim of continuing with the leaching on the residue of fraction 1, the difficulty of drying the residue without the use of any heating-vacuum treatment leads us to maintaining the residue wet.

Consequently, our option was to employ an internal standard, which quantifies the metals still retained by the wet residue. The recovery value of the internal standard in each extract allows the evaluation of the possible loss. One standard of metal was used as an internal standard in each fraction of the speciation scheme: caesium in the first fraction; gallium in the second fraction; indium in the third fraction; gold in the

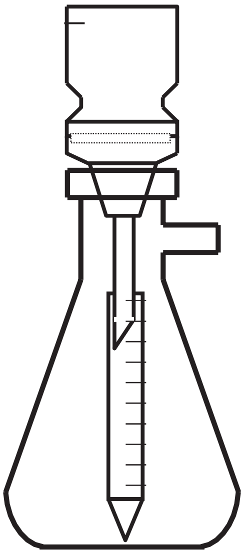

Figure 3. The conical tube used to measure the extract of solutions is placed into the apparatus of filtration just down the exit of the porous filter of the membrane in order to avoid loss or contamination of solutions due to the transfer from the suction flask.

fourth fraction. The elements selected must be absent in the air and must be soluble salts that do not precipitate metals in each extractable solution. The absence of these elements in airborne particles was verified by an analysis of different filters collected during long periods, so they were highly loaded with particulate matter. In spite of this selection, other elements could be selected in other special sites of the world. These filters were obtained by long sampling periods, collecting particles from 6:00 to 15:00 h and from 16:00 to 22:00 h for 1 week. All values measured for the four internal standards were below the detection limit of the method.

Four clean filters were spiked with a standard of metals and submitted to the microwave programme with the acid mixture. Two of the four filters were submitted to the microwave programme without the use of internal standards, and the other two were submitted to the microwave programme with the gold standard. The use of the internal standard of gold demonstrated that it was a useful tool to correct the loss of metal concentrations. Finally, two other filters were submitted to the complete scheme using the four internal standards, in order to check that this modification was adequate for this.

3.5 Acid mixture for microwave assistance

For acid digestion, the speciation scheme tested in 1994–1995 used an acid $HNO_3 : HCl$ mixture (5 : 2) and diluted with 20 mL of deionized water in Erlenmeyer flasks. The speciation scheme optimized in 1996–1997 used a 6 : 2 : 5 $HNO_3 : HCl : HClO_4$ mixture in polypropylene centrifugal tubes. Accordingly, for acid digestion in PTFE vessels of a microwave system, three different acid mixtures were tested in order to obtain the best recoveries.

The different mixtures were tested twice, first on two real samples (table 4) and finally verified on the SRM 1648 reference material. Ten millilitres of each mixture were added to each vessel containing a twelfth of the filter. After cooling, observations discarded certain mixtures. The vessels containing the nitric–sulphuric mixture gave off yellow vapours. These vapours indicate the possible loss of volatile elements from the extracted solution. In addition, sulphate causes lead precipitation (table 5). The residue submitted to the nitric–hydrochloric mixture was not completely decoloured as in the other vessels. Black particles stayed in the filter pieces, indicating incomplete acid digestion. Additionally, low arsenic recoveries were found in this mixture. The nitric–perchloric mixture was the only one to reach the highest recoveries. Thus, the final acid mixture $HNO_3 : HClO_4$, 3 : 1, was selected and validated with the SRM 1648 urban dust material reference (table 5). The final scheme improved in 2004 is presented in table 6.

Table 4. Results of the test of the three acid mixtures on real samples.

Test	Acid mixture (3 : 1)	As (mg g^{-1})	Hg (mg g^{-1})	Pb (mg g^{-1})	Cd (mg g^{-1})	Ni (mg g^{-1})
1	HNO_3/H_2SO_4	55.1	6.7	102.7	63.3	126.4
2	HNO_3/H_2SO_4	62.2	4.5	156.6	65.5	121.4
3	$HNO_3/HClO_4$	72.5	13.0	2708.1	94.6	176.8
4	$HNO_3/HClO_4$	67.1	7.0	2845.2	113.5	174.7
5	HNO_3/HCl	38.1	7.4	2441.5	110.2	182.8
6	HNO_3/HCl	48.7	9.9	2072.5	112.2	188.2

Table 5. Results of validation using the SRM 1648 (urban dust) material reference.

Element	Recovery (%) ($n = 18$)	RSD ($n = 18$)	Confidence level ($p = 0.05$)	AOAC interval
As	99.9	6.7	3.3	90–107
Se	74.3	17.3	8.6	80–110
Pb	95.3	2.6	1.3	95–105
Cd	110.0	3.7	1.8	80–110
Ni	86.0	4.2	2.1	80–110
Mn	98.9	2.3	1.1	90–107
Fe	102.2	2.1	1.0	97–103
Cr	38.5	1.7	0.8	90–107
V	80.5	2.5	1.2	90–107
Cu	92.1	1.3	0.6	90–107

Table 6. Final speciation scheme improved in 2004.

Metallic fraction	Reagent	Experimental conditions
1. Soluble and exchangeable metals	22 mL H_2O (pH 7.4)	3 h at room temperature; shaker agitation
2. Carbonates, oxides and reducible metals	16 mL $NH_2OH \cdot HCl$ 0.25 M at pH 2	5 h at room temperature; shaker agitation
3. Bound to organic matter, oxidizable and sulphidic metals	7.5 mL H_2O_2 30% + 20 mL NH_4AcO 2.5 M at pH 3	In microwave + 90 min at room temperature; shaker agitation
4. Residual metals	15 mL $HNO_3 : HClO_4$ (3 : 1)	In microwave

4. Conclusions

The new operational scheme for determination of chemical speciation has been released from hard operations that usually contributed to non-reproducible results. The main advances involving the use of microwave assistance, the best centrifugation programme, filtration of particles separated from filters, internal standards, and an optimum acid mixture allow for an easy and accurate performance of the operational leaching. The aim of the work can be considered fulfilled, and at the present workshop, our chemical speciation scheme was presented and proposed as a useful method and a relevant contribution for consideration by the international community.

Acknowledgements

The authors thank the Regional Ministry of the Environment of the Andalusian Government (Consejeria de Medio Ambiente de la Junta de Andalucia) for financial assistance.

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