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Comparative study of pretreatment methods for the determination of metals in atmospheric aerosol by electrothermal atomic absorption spectrometry

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Abstract

A comparative study of pretreatment methods for the determination of 10 elements (As, Cd, Pb, V, Ni, Mn, Cr, Cu, Fe, Al) in atmospheric aerosols by electrothermal atomic absorption spectrometry (ETAAS) was conducted. For the digestion of the particulates collected in filters, six methods were compared using a mixture of HNO_3 and HF with or without the addition of various oxidative agents ($HClO_4$ or H_2O_2) or acids (HCl). The comparative study was performed using loaded cellulose filter samples, which were digested in Parr bombs and heated in a conventional oven at 170 °C for 5 h. The extraction efficiency and blanks were compared and it was proved that the digestion method using only HNO_3–HF extracted most of the metals and gave the lowest blanks. The HNO_3–HF mixture was selected for the development of an improved microwave digestion method specific for aerosol-loaded filters. The operating parameters were optimized, so that quantitative recovery of the reference materials NIST 1649a urban dust and NIST 1648 urban particulate matter was achieved. The blank of cellulose and teflon filters were also determined and compared. Teflon filters present the lowest blanks for all the elements. The obtained limits of detection for each type of filters were adequate for environmental monitoring purposes. ETAAS instrumental operation was also optimized for the compensation and the elimination of interferences. The temperature optimization was performed for each metal in every type of filter and optimized parameters are proposed for 10 elements.

Keywords: Airborne particulate matter; Fine particles; Metals; Digestion; Teflon filters; Cellulose filters; ETAAS

1. Introduction

Determination of metal and metalloid content in the atmospheric aerosols is of great interest, due to their adverse effects on human health [1]. European Commission legislation obliges member states to monitor the lead content in atmospheric particulates [2]. Recently, acknowledging that other metals in the air have detrimental effect on the human health, it was proposed that cadmium, arsenic and nickel should also be monitored in atmospheric particulate matter [3]. This proposal is expected to be adopted by member states in the immediate future. These two documents state that these elements should be determined in atmospheric aerosols (PM_{10} and $PM_{2.5}$) and propose atomic absorption spectrometry as one of the reference methods for these determinations.

Many studies have already been published on the preparation of atmospheric particulate samples for chemical analysis. Two main techniques have been used: digestion and extraction. In the case of chemical analysis of airborne lead collected on filters, an international standard has been developed which specifies a method based on acid digestion and atomic absorption spectrometry [4]. However, airborne particulate matter collected on membrane filters has been con-

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Table 1
Temperature program for the determination of seven metals (V, Ni, Cr, Mn, Cu, Fe, Al) with standard pyrolytic graphite furnace

	Step								
	1	2	3	4	5	6	7	8	9
T (°C)	85	120	120	$T_{pyr.}$ [a]	$T_{pyr.}$ [a]	$T_{pyr.}$ [a]	$T_{at.}$ [a]	$T_{at.}$ [a]	2700
t (s)	5	20	10	$t_{pyr.}$ [b]	$t_{pyr.}$ [b]	$t_{pyr.}$ [b]	$t_{at.}$ [c]	$t_{at.}$ [c]	2

[a] Atomization temperatures ($T_{at.}$) and pyrolysis temperatures ($T_{pyr.}$) are given in Table 3.
[b] Time values for pyrolysis steps ($t_{pyr.}$): 5/2/2 s for Mn, Cr, Fe, Cu, Ni; 5/11.9/2 s for Al and 5/5/2 s for V.
[c] Time values for atomization steps ($t_{at.}$): 1.1/2 s for Cr, Mn, Fe, Ni; 0.8/2.5 s for Cu, Al and 0.9/3 s for V.

Table 2
Temperature program for the determination of three elements (As, Cd, Pb) with pyrolytic graphite furnace L'vov platforms

	Step								
	1	2	3	4	5	6	7	8	9
T (°C)	120	200	200	$T_{pyr.}$ [a]	$T_{pyr.}$ [a]	$T_{pyr.}$ [a]	$T_{at.}$ [a]	$T_{at.}$ [a]	2500
t (s)	5	30	10	$t_{pyr.}$ [b]	$t_{pyr.}$ [b]	$t_{pyr.}$ [b]	$t_{at.}$ [c]	$t_{at.}$ [c]	2

[a] Atomization temperatures ($T_{at.}$) and pyrolysis temperatures ($T_{pyr.}$) are given in Table 3.
[b] Time values for pyrolysis steps ($t_{pyr.}$): 10/5/2 s for Pb, As and 5/5.2/3.2 s for Cd.
[c] Time values for atomization steps ($t_{at.}$): 1/2.5 s for As, 1/3.1 s for Pb and 0.8/4.7 s for Cd.

Table 3
Atomization temperatures ($T_{at.}$) and pyrolysis temperatures for aqueous standards ($T_{pyr.(aq.)}$), cellulose filter ($T_{pyr.(cel.)}$) and teflon filter ($T_{pyr.(teflon)}$)

Element (°C)	As	Cd	Pb	V	Ni	Cr	Mn	Cu	Fe	Al
$T_{pyr.(aq.)}$	600	600	800	1400	800	1200	800	800	900	1300
$T_{pyr.(cel.)}$	650	450	750	1200	1000	1200	600	750	700	1200
$T_{pyr.(teflon)}$	650	600	500	1300	900	1200	800	500	600	1100
$T_{at.}$	2400	1800	2300	2700	2400	2600	2400	2300	2300	2500

sidered as a difficult-to-digest sample, because it contains a variety of matrix constituents, such as organics, oxides and silicates. Therefore, the acidic decomposition prior to final determination is considered to be the critical step of this analytical methodology [5]. Due to the small amount of atmospheric particles collected on filters (a few milligrams), the preferable method for trace element analysis is total digestion [6]. Various methods have been proposed in the literature, using different heating methods, working acid mixtures and digestion time [7–14]. The mixture of HNO_3–HCl is often used in routine analysis, giving recoveries >90% for metals, such as Pb and Cd [15,16]. However, their recoveries are not constant between samples, [7] and acid mixtures which contain HF are considered mandatory for improving digestion recovery [7,17–19]. During the last decade microwave digestion is receiving considerable attention and use in the laboratory [20]. Wet digestion procedures with conventional heating are usually slow and are subject to possible contamination and potential loss of some volatile elements. Microwave-assisted digestion has the advantages of reduced time for sample dissolution, use of less chemicals and lower losses of some volatile elements [18–24]. EPA suggests microwave acid digestion of complex matrices using a mixture of HNO_3–HF as a rapid and effective multielement method [21]. However, a reference-validated method that can be used for the determination of various metals and for the digestion of various types of filters is not available in literature.

The aim of this study was the comparison of various digestion methods of filters (teflon or cellulose filters), which are used for sampling airborne particulate matter ($PM_{2.5}$), prior to the determination of 10 elements by electrothermal atomic absorption spectrometry (ETAAS). The comparison of these methods was first performed for the case of samples heated into Parr bombs in a conventional oven. Blank values and recovery of metals for a certified reference material was used in order to assess the performance of the digestion method. Special attention was paid to the improvement of the suggested digestion method. On this basis, an optimized microwave digestion method was also developed and validated. Methods which can be used in any environmental analysis laboratory were proposed for 10 elements.

2. Materials and methods

2.1. Instrumentation

A Varian 220 spectrometer equipped with a GTA 110 graphite furnace and a Varian autosampler was used for elemental analysis. Hollow cathode lamps were used as radiation sources for all the elements. The recommended Varian instrumental parameters were used. ETAAS conditions were carefully optimized for the compensation or elimination of interferences. The optimized temperature programs are given in Tables 1–3. Pyrolysis temperature was

influenced by the filter matrix (Table 3). Thus, temperature optimization was performed for each metal in every type of filter.

Size-resolved aerosol samples were collected on cellulose filters using a six-stage Andersen cascade impactor at a flow rate of 20 cf min^{-1} operating continuously for 24 h. The particle size range collected from impactor stages are >10.2, 10.2–4.2, 4.2–2.1, 2.1–1.4, 1.4–0.73 and 0.73–0.41 μm. An additional back-up filter is placed at the end of the impactor outlet to collect particles of size <0.41 μm.

$PM_{2.1}$ custom-made sampling head, operating at 23 l min^{-1}, was employed to collect particles with diameter <2.1 μm on teflon filters [25].

Teflon filters were obtained from Whatman with pore size 1 μm and cellulose filters were Whatman 41 paper sheets (8 in. × 10 in.).

The digestion of samples was carried out by means of (i) a conventional oven Gallencamp equipped with Parr bombs and (ii) a domestic microwave oven of a maximum power 1000 W, using either PFA vessels (60 ml) resistant up to 100 psi from Savillex or PFA vessels (85 ml) resistant up to 600 psi from O.I. Analytical (O.I. Corporation).

2.2. Reagents

Concentrated HNO_3 65%, HF 40%, HCl 30% and H_2O_2 30% were of suprapur grade (Merck) whereas $HClO_4$ 70% was of proanal grade (Merck). Titrisol stock standard solutions of metals (1000 mg l^{-1}) were obtained from Merck. Palladium (as Pd, 10 g l^{-1}) and Mg (as $Mg(NO_3)_2$, 10 g l^{-1}) modifiers were of suprapur grade and obtained from Merck. Certified reference materials SRM Urban Dust 1649a and particulate matter SRM 1648 from NIST were used for validation purposes.

2.3. Procedure

2.3.1. Conventional digestion

Six digestion methods were compared for the digestion of atmospheric particles collected on cellulose filters.

- Method 1: 3.00 ml HNO_3 + 1.25 ml $HClO_4$ + 1.00 ml HF
- Method 2: 2.50 ml HNO_3 + 0.50 ml $HClO_4$ + 1.00 ml HF
- Method 3: 2.50 ml HNO_3 + 0.20 ml $HClO_4$ + 1.00 ml HF
- Method 4: 2.00 ml HNO_3 + 2.00 ml HCl + 1.00 ml HF
- Method 5: 2.00 ml HNO_3 + 2.00 ml H_2O_2 + 1.00 ml HF
- Method 6: 2.00 ml HNO_3 + 1.00 ml HF

Samples were placed in teflon vessels, the appropriate acid mixture was added, the vessels were fitted in Parr bombs and heated in a conventional oven at 170 °C for 5 h. After digestion and cooling, the samples were diluted at 10.0 ml with ultra pure water (millipore). All the metals were determined without further dilution, except for Fe and Al determinations in which the digested samples were diluted 100 times. The study was aimed at the higher recovery of the digestion method and the lower blank value for the following metals elements: As, Cd, Pb, V, Ni, Cr, Mn, Cu, Fe, Al. One microgram of Pd was used as chemical modifier for the determination of Cd, As and Pb, whereas 10 μg of Mg (as $Mg(NO_3)_2$) was used in the determination of V.

The most effective conventional method (method 6) was validated. Quantification was conducted using either standard or matrix-matched calibration curves. The following range of concentrations for each metal were injected in triplicate: 20–80 μg l^{-1} of As, 0.40–1.0 μg l^{-1} of Cd, 20–80 μg l^{-1} of Pb, 20–80 μg l^{-1} of V, 5.0–40 μg l^{-1} of Ni, 1.5–4.5 μg l^{-1} of Mn, 10–40 μg l^{-1} of Cr, 5–40 μg l^{-1} of Cu, 5.0–15 μg l^{-1} of Fe and 10–40 μg l^{-1} of Al.

The limit of detection (LOD) was determined as three times the standard deviation of 10 replicates of the procedural blank. Repeated spike tests ($n = 3$) of multi-element standard solution on blank cellulose and teflon filters were performed to assess the recovery of the method. The reference material NIST 1649a urban dust was used for the validation of the proposed method.

2.3.2. Microwave digestion

A conventional microwave oven, with a maximum power of 1000 W was used for the development of the microwave digestion method. At the beginning, Savillex PFA vessels (60 ml) equipped with a pressure relief mechanism were used for the microwave digestion procedure. Prior to their use, teflon vessels were first sonicated for 15 min and then soaked in 10% HNO_3 overnight to ensure cleaning and to prevent contamination from the vessels. After being rinsed with ultra pure water, the vessels were filled with 5 ml HNO_3 65% and treated in the microwave oven under the same conditions as used for the sample digestion. After being cooled, they were flushed once more with ultra pure water [12,23]. In order to find the optimum microwave program, several programs were tested with various combinations of power setting and digestion time. While attempting to achieve the complete digestion of the particulate matter, sample losses were observed at power settings over 450 W. Low recoveries of trace elements and condensation of acid droplets on the external part of the vessels confirmed this effect [10].

Table 4A shows the optimum microwave program settings using Savillex vessels. Cellulose filters (Whatman 41), loaded with the reference material (approximately 10 mg)

Table 4
Program setting of microwave digestion of airborne particulate matter (A) with Savillex and (B) with O.I. Analytical vessels

Microwave digestion step	Microwave power (W)	Time (min)
(A) Savillex vessels		
1	150	4
2	300	2
3	450	2
(B) O.I. Analytical vessels		
1	300	5
2	450	2
3	600	2

Table 5
Concentrations of trace elements in one blank cellulose filters in $\mu g\,l^{-1}$ (n = 3) for each digestion method

Element	Method 1	Method 2	Method 3	Method 4	Method 5	Method 6
As	7.88	6.50	6.23	4.10	4.48	2.76
Cd	0.14	0.051	0.057	0.10	0.045	0.020
Pb	3.53	1.26	1.65	2.06	1.56	0.57
V	0.48	0.78	0.52	1.05	0.72	0.44
Ni	0.51	0.84	1.66	1.86	0.78	0.36
Cr	6.19	1.19	1.45	1.70	1.40	0.75
Mn	0.90	0.70	0.34	0.66	0.96	0.26
Cu	0.88	1.02	0.72	1.25	0.93	0.75
Fe[a]	3.49	2.05	2.53	2.72	2.22	1.81
Al[a]	9.51	2.06	2.76	2.04	2.73	1.79

[a] 100-fold diluted.

were placed in the closed vessels and digested using method 6 in the microwave oven with the program setting shown in Table 4A. The reference material NIST 1649a urban dust was used for the validation of the proposed method.

It became evident that the particular configuration of the Savillex PFA vessels used in the study, was inadequate to withstand the pressure resulting from the amount of sample and acid mixture required for quantitative analysis. An alternative type of PFA vessel (O.I. Analytical) capable of withstanding pressures of up to 600 psi was used. Table 4B shows the optimum program setting for O.I. Analytical vessels. The reference material NIST 1648 particulate matter was used for the validation of the proposed method.

For each procedure, blank filters (teflon and cellulose) were analyzed. Then, the limits of detection (LODs) were determined as three times the standard deviation of the procedure blank.

3. Results and discussion

3.1. Preliminary investigations and optimization of the conventional digestion procedure

Method 6, which uses only HNO_3–HF, was proved to extract the most of the studied metals effectively from fine and coarse particles collected on cellulose filters. Methods 4 and 5 were insufficient for the extraction of most of the metals (results are not shown). Hydrofluoric acid is needed for the dissolution of silicates and allows better recoveries for elements such as Cr and Ni. For Cu, Mn, Pb the use of hydrofluoric acid does not improve their recovery, a result which was also reported in the literature [10,12]. A study conducted by Wang et al. [13] on the efficiency of acids for the digestion of urban particulate matter proposes the use of an acid mixture containing perchloric acid as a powerful oxidant needed to dissolve organic matter. However, blank values for some metals (Cd, As, Pb, Mn, Fe, Al, Cr) increased with increasing amount of $HClO_4$ (Table 5). Method 6 gave lower blank values than the methods that use $HClO_4$. The presence of perchloric acid during sample digestion can result in the formation of explosive perchlorates, and when possible, the use of $HClO_4$ should be avoided.

3.2. Validation of the conventional digestion procedure

In order to investigate possible interference from the digested matrix for each type of filter, the slopes of standard calibration equations (SC), derived from aqueous standards, were compared with the slopes of matrix-matched calibration equations (SAC), derived from standard additions in the extract of a real sample for each type of filter. The results are presented in Table 6. Digestion method 6 was used. Significant statistical differences between the slopes of the calibration curves were tested using t-test. The only significant difference in sensitivity was observed in the case of As and V determination in cellulose filters. In all the other cases, SAC slopes do not differ significantly from SC slopes. Therefore, it was decided to use aqueous standard calibration curves for quantification, except for As and V determination in cellulose filters.

Repeated spike tests (n = 3) of multi-element standard solution on blank cellulose and teflon filters were performed, using the HNO_3–HF conventional digestion. The recoveries, which were calculated from standard calibration curves, except for V and As where matrix-matched calibration was used, are satisfactory and are given in Table 7. Table 7 shows that all elements had recoveries between 91 and 115%.

Table 6
Comparison of the slopes of standards calibration equations (SC) with the slopes of matrix-matched equations (SAC) (mean ± S.D., n = 5 different days)

Element	Slope SC	Slope SAC (cellulose)	Slope SAC (teflon)
As	0.0014 ± 0.00012	0.0019 ± 0.00019[a]	0.0012 ± 0.00015
Cd	0.0833 ± 0.0067	0.0833 ± 0.0066	0.0833 ± 0.0069
Pb	0.00199 ± 0.00014	0.00189 ± 0.00021	0.00209 ± 0.00011
V	0.00157 ± 0.00011	0.00112 ± 0.00035[a]	0.00148 ± 0.00020
Ni	0.00424 ± 0.00047	0.00478 ± 0.00065	0.00446 ± 0.00024
Mn	0.0175 ± 0.0028	0.0194 ± 0.0035	0.0201 ± 0.0016
Cr	0.0152 ± 0.00016	0.0150 ± 0.00019	0.0149 ± 0.00019
Cu	0.00658 ± 0.00056	0.00654 ± 0.00052	0.00645 ± 0.00067
Fe	0.00692 ± 0.00035	0.00650 ± 0.00072	0.00659 ± 0.00048
Al	0.00232 ± 0.00044	0.00232 ± 0.00037	0.00235 ± 0.00046

[a] Value statistically significant difference at P = 0.05.

Table 7
Recovery results (%) from spike tests

	Element									
	As	Cd	Pb	V	Ni	Mn	Cr	Cu	Fe	Al
Teflon	97 ± 1	100 ± 2	91 ± 5	97 ± 2	102 ± 2	96 ± 6	100 ± 1	93 ± 6	112 ± 10	96 ± 4
Cellulose	96 ± 5	106 ± 10	97 ± 3	95 ± 2	114 ± 2	98 ± 4	101 ± 4	104 ± 6	100 ± 8	115 ± 14

Three additions for each metal in blank filters in the range of 0.20–40 μg l^{-1}, three replicates per addition, $n = 3 \times 3$.

Table 8
Limit of detection (LOD, μg l^{-1}) and injection reproducibility (S_R %) for each metal determination by ETAAS

	Element									
	As	Cd	Pb	V	Ni	Mn	Cr	Cu	Fe	Al
LOD (μg l^{-1})	2.26	0.025	1.16	1.23	0.46	0.25	0.50	1.50	0.50[a]	6.0[a]
S_R (%)[b]	1.2	0.8	2.2	0.9	1.0	1.1	1.8	1.2	2.5	9.5

[a] 100-fold diluted.
[b] Concentrations (μg l^{-1}) Cd: 0.60; Pb: 12.0; V: 10.0; Ni: 9.0; Cr: 16.0; Mn: 4.50; Cu: 8.0; Fe: 9.0; Al: 30.0.

The limit of detection (LOD) and the injection reproducibility (as S_R %, $n = 3$) for each element were determined. LODs were obtained as three times the standard deviation of the blanks from cellulose filters and aqueous standard calibration curves (SC), except for As and V determination, where matrix-matched calibration curves were used. The results are given in Table 8. One can observe that LOD and S_R % of Al are higher than the expected values, due to the high value and great variability in the blank of the method.

In order to determine the trueness and precision of the suggested digestion procedure (2.00 ml HNO_3 + 1.00 ml HF) for particulate samples, the certified reference material NIST SRM 1649a urban dust was used. Although NIST recommends using at least 100 mg of this material in order to minimize variation due to sample inhomogeneity, we obtained good precision with much smaller sample size of approximately 10 mg. The results of this study are presented in Table 9. Reproducibility of the method (S_R %, two replicates, $n = 2$, at three different days, $k = 3$) is also shown in Table 9. Al is not certified and therefore is not determined. The agreement between experimental and certified value was satisfactory for Cd, Pb, Ni, Cu and Fe. The contents of some elements (As, Mn) are significantly higher than the NIST value probably due to sample contamination. Reduced recoveries were obtained for Cr and V due to their incomplete dissolution. Probably more rigorous digestion conditions are needed to achieve complete recovery of these metals. Thus, a microwave digestion procedure was tried and optimized.

3.3. Validation of microwave digestion method

The microwave digestion method using Savillex vessels was then validated. Cellulose filters, loaded with the reference material NIST 1649a (approximately 10 mg), were placed in the closed digestion vessels (Savillex) and digested using Method 6 in the microwave oven with the digestion program setting shown in Table 4A. Quantification was performed by using aqueous standards calibration curves. For As and V determination in cellulose filters, matrix-matched calibration curves were used. Experimental values and certified values were compared to evaluate the analytical accuracy. Results are shown in Table 10. The higher value for

Table 9
Elemental content results (in μg g^{-1}, $n = 2$, $k = 3$) of the certified reference material 1649a urban dust (NIST) digested by the conventional procedure and the obtained reproducibility (S_R, %)

Element	Certified value (μg g^{-1})	Measured value[a] (μg g^{-1})	S_R (%)
As	67 ± 2	108 ± 10	9.3
Cd	(22)[c]	24 ± 2	8.3
Pb[b]	1.24 ± 0.04	1.20 ± 0.03	2.5
V	345 ± 13	173 ± 15	8.7
Ni	166 ± 7	174 ± 8	4.6
Mn	237 ± 8	330 ± 6	1.8
Cr	211 ± 6	130 ± 8	6.2
Cu	223 ± 7	254 ± 7	2.8
Fe[b]	2.98 ± 0.07	3.1 ± 0.1	3.9

[a] Mean ± S.D. ($n \times k = 6$).
[b] Content in weight percentage (% w/w).
[c] Information value.

Table 10
Elemental contents (in μg g^{-1}, $n = 2$, $k = 3$) of certified reference material NIST 1649a urban dust dissolved by microwave assisted digestion using Savillex vessels and the obtained reproducibility (S_R %)

Element	Certified value (μg g^{-1})	Measured value[a] (μg g^{-1})	S_R (%)
As	67 ± 2	96 ± 8	8.3
Cd	(22)[c]	20 ± 2	10.0
Pb[b]	1.24 ± 0.04	1.10 ± 0.06	5.5
V	345 ± 13	333 ± 12	3.6
Ni	166 ± 7	176 ± 8	4.5
Mn	237 ± 8	296 ± 3	1.0
Cr	223 ± 7	245 ± 5	2.0
Cu	211 ± 6	199 ± 6	3.0
Fe[b]	2.98 ± 0.07	2.8 ± 0.2	7.1

[a] Mean ± S.D. ($n \times k = 6$).
[b] Content in weight percentage (% w/w).
[c] Information value.

Table 11
Elemental contents (in $\mu g\,g^{-1}$, $n = 2$, $k = 3$) of certified reference material NIST 1648 particulate matter dissolved by microwave-assisted digestion using O.I. Analytical vessels and the obtained reproducibility (S_R %)

Element	Certified value ($\mu g\,g^{-1}$)	Measured value[a] ($\mu g\,g^{-1}$)	S_R (%)
As	115 ± 10	160 ± 14	8.8
Cd	75 ± 7	72 ± 6	8.3
Pb[b]	0.655 ± 0.008	0.598 ± 0.010	1.7
V	127 ± 7	121 ± 7	5.8
Ni	82 ± 3	89 ± 4	4.5
Mn	786 ± 17	875 ± 19	2.2
Cr	403 ± 12	389 ± 10	2.6
Cu	609 ± 27	583 ± 14	2.4
Fe[b]	3.9 ± 0.1	3.7 ± 0.3	8.7
Al[b]	3.4 ± 0.1	3.8 ± 0.5	13.2

[a] Mean ± S.D. ($n = 3$).
[b] Content in weight percentage (wt.%).

As and Mn could be contamination problem from the laboratory environment. However, this was not observed when blank filters were analyzed (see Table 12). For all the other metals, plus Cr and V, the recoveries were quantitative and the applied method can efficiently extract the metals from the particulates.

However, Savillex vessels were replaced by O.I. Analytical vessels, which can withstand higher pressures (up to 600 psi). Therefore, the microwave digestion method was adjusted to the new conditions that could be applied. Certified reference material from NIST particulate matter 1648 was used for the determination of the microwave extraction efficiency of all metals plus Al. The procedure described above was followed using the digestion program setting shown in Table 4B. Results are shown in Table 11. For most of the elements satisfactory agreement between measured and certified values was found. Reproducibility of the method (S_R, two replicates, $n = 2$, at three different days, $k = 3$) is also shown in Tables 10 and 11. Reproducibility lower than 10% was found for all the metals except Al, where a S_R value of 13% was obtained.

A parameter important to determine is the mean value of blanks to make accurate blank subtraction especially at low levels of analyte in the sample. LODs in air samples are greatly influenced by the blank values for the filters. In order to assess any possible contamination from water, acids, vessels and bottles, reagent blank tests were carried out. The reagent blank was composed of deionized water and the same amounts of acids as those used in microwave digestion procedure. For all elements, results were below instrumental detection limit. Furthermore, 10 blank cellulose and 10 teflon filters (approximately 50 mg each) were digested with the proposed mixture (HNO_3–HF) in the microwave oven. Tables 12 and 13

Table 12
Contents of trace elements in blank cellulose filters in $\mu g\,l^{-1}$ and $\mu g\,g^{-1}$ and the respective method detection limits in $ng\,m^{-3}$ ($n = 10$), $V_{air} = 700\,m^3$

Element	Cellulose blank ($\mu g\,g^{-1}$)	Cellulose blank in solution ($\mu g\,l^{-1}$)	Detection limit in solution ($\mu g\,l^{-1}$)	Detection limit in air with cellulose filters ($ng\,m^{-3}$)
As	0.7 ± 0.1	3.6 ± 0.5	1.50	0.021
Cd	0.030 ± 0.002	0.15 ± 0.01	0.03	0.0004
Pb	0.9 ± 0.1	4.2 ± 0.5	1.50	0.021
V	0.10 ± 0.01	0.50 ± 0.07	0.21	0.003
Ni	0.46 ± 0.02	2.30 ± 0.09	0.27	0.004
Mn	1.33 ± 0.09	6.6 ± 0.4	1.32	0.019
Cr	1.3 ± 0.1	6.5 ± 0.5	1.56	0.022
Cu	1.1 ± 0.1	5.6 ± 0.5	1.44	0.021
Fe	180 ± 8	9.0 ± 0.4[a]	1.20[a]	1.7
Al	800 ± 20	40 ± 1[a]	3.00[a]	4.3

[a] 100-fold diluted.

Table 13
Contents of trace elements in blank teflon filters in $\mu g\,l^{-1}$ and $\mu g\,g^{-1}$ and the respective method detection limits in $ng\,m^{-3}$ ($n = 10$), $V_{air} = 30\,m^3$

Element	Teflon blank ($\mu g\,g^{-1}$)	Teflon blank in solution ($\mu g\,l^{-1}$)	Detection limit in solution ($\mu g\,l^{-1}$)	Detection limit in air with teflon filters ($ng\,m^{-3}$)
As	0.56 ± 0.08	2.8 ± 0.4	1.20	0.40
Cd	0.020 ± 0.001	0.100 ± 0.005	0.015	0.005
Pb	0.56 ± 0.06	2.8 ± 0.3	0.9	0.03
V	0.100 ± 0.008	0.50 ± 0.04	0.12	0.004
Ni	0.300 ± 0.006	1.48 ± 0.03	0.09	0.03
Mn	0.52 ± 0.06	2.6 ± 0.3	0.90	0.30
Cr	0.82 ± 0.08	4.1 ± 0.4	1.20	0.40
Cu	0.76 ± 0.06	3.8 ± 0.3	0.9	0.30
Fe	6 ± 1	3.0 ± 0.5[a]	1.5[a]	5
Al	31 ± 2	16 ± 1[a]	3.0[a]	10

[a] 10-fold diluted.

summarize the contents ($\mu g\, g^{-1}$) of trace elements in blank cellulose and teflon filters, respectively. The teflon filters gave the lowest blank values for all the elements studied. It is obvious that the filter contribution in blank values is negligible for most of the metals. The exceptions are Fe and Al. These elements show high blank values in cellulose as it was expected [24]. However, this is not a problem for atmospheric aerosol samples, as the concentrations of Fe and Al are well above these levels. Tables 12 and 13 also show the detection limits in solution of trace metals based on 10 replicates of the filter blank. The detection limits were also expressed in terms of weight of an element per finite air volume ($ng\, m^{-3}$). It is assumed that the volume of sampled air in case of cellulose filters was $700\, m^3$ and the volume of sampled air in case of teflon filters was $30\, m^3$. LODs obtained in this work for cellulose filters were similar to those reported in previous studies [12,24].

4. Conclusions

A comparative study for the determination of 10 elements in atmospheric aerosols by ETAAS was conducted. The acid mixture, which contained only HNO_3–HF, was proved to extract the studied metals effectively from teflon and cellulose filters. The addition of perchloric acid increased blank values for most of the metals. Therefore, perchloric acid was not used. A conventional digestion procedure and a microwave digestion procedure using a domestic microwave oven and PFA vessels resistant up to 600 psi were developed and validated. Recovery studies were conducted using two certified reference materials, NIST SRM 1648 Urban Particulate Matter and NIST 1649a urban dust. The LODs for both cellulose and teflon filters were satisfactory and adequate for environmental monitoring and similar to those reported in previous studies. Teflon filters presented significantly lower blanks. The results of these studies showed that microwave digestion with HNO_3–HF is an effective and the preferable pretreatment method for the determination of trace elements in airborne particles.

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Further reading

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