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Comparison of three different sample preparation procedures for the determination of traffic-related elements in airborne particulate matter collected on glass fiber filters

Ivan N.B. Castilho[a], Bernhard Welz[a,b,*], Maria Goreti R. Vale[b,c], Jailson B. de Andrade[b], Patricia Smichowski[d], Abdallah A. Shaltout[a,e], Lígia Colares[a], Eduardo Carasek[a]

[a] *Departamento de Química, Universidade Federal de Santa Catarina, 88040-900 Florianópolis, SC, Brazil*
[b] *Instituto Nacional de Ciência e Tecnologia do CNPq, INCT de Energia e Ambiente, Universidade Federal de Bahia, 40170-115 Salvador, BA, Brazil*
[c] *Instituto de Química, Universidade Federal do Rio Grande do Sul, 91501-970 Porto Alegre, RS, Brazil*
[d] *Comisión Nacional de Energia Atómica, B1650KNA-San Martín, Pcia de Buenos Aires, Argentina*
[e] *Spectroscopy Department, Physics Division, National Research Center, El Behooth Str., 12622 Dokki, Cairo, Egypt*

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ABSTRACT

Three different procedures for sample preparation have been compared for the determination of Cu, Mo and Sb in airborne particulate matter (APM) collected on glass fiber filters using high-resolution continuum source graphite furnace atomic absorption spectrometry (HR-CS GF AAS). Direct solid sample analysis of the ground filters was compared with microwave-assisted acid leaching with *aqua regia* and ultrasound-assisted extraction also using *aqua regia*. The main absorption line at 324.754 nm or the secondary line at 216.509 nm was used for the determination of Cu, depending on the analyte content in the samples. The primary absorption line at 313.259 nm was used for Mo and the secondary line at 212.739 nm for Sb determination. The limits of detection (LOD, 3σ) found for the direct solid sampling method, based on ten atomizations of an unused filter were 15 $\mu g\,g^{-1}$ for all three analytes, corresponding to 40 $ng\,m^{-3}$ for a typical air volume of 1440 m^3 collected over a period of 24 h. The LOD for the other two methods were less than a factor of two inferior, but the total time required for an analysis was significantly longer. The repeatability of the measurements was between 3 and 9% ($n = 5$), and the results obtained with the three methods did not show any significant difference. The ratio between the three analytes on the filters from areas of intense traffic was found to be around Cu:Mo:Sb ≈ 4:1:1.4, which suggests that the source of all three elements is brake linings, i.e., related to automobile traffic. When the ratio deviated significantly from the above values, the source of contamination was assumed to be of different origin.

1. Introduction

Man-made pollution is of concern to the society as a whole and efforts are made nowadays worldwide to minimize its effects on the global population and on climate changes. The major source of anthropogenic pollution since the industrial revolution is burning of fossil fuels, and automobile traffic has a significant contribution to that, at least in highly populated areas. The main concern associated with pollution due to automobile traffic is the production of the green-house gases CO and CO_2, and gases related to acid rain, such as NO_x and SO_2. However, even if this is indeed the most problematic pollution, the vehicles also release particles into the atmosphere, such as soot, and through other means such as brake pads, tires, road surface, re-suspension of soil and road dust [1]. As a consequence, new challenges have been posed to human health and the environment by emerging pollutants, the importance of which was recognized only recently.

In this context, more efficient and reliable analytical controls have been solicited by environmental agencies and governmental offices in different countries, where programs for monitoring particle emission and the presence of metals and metalloids in air particulate matter (APM) have been established. Formulation of cost-effective air pollution control policies depends on a sound knowledge of source contribution to ambient concentrations. Epidemiological and toxicological studies provide documented evidence of an increase in morbidity, or even fatalities, with the exposure to exceedingly high levels of toxic elements such as As, Cd, Cr, Ni, Pb and Sb in the inhalable fractions of APM [1].

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* Corresponding author at: Departamento de Química, Universidade Federal de Santa Catarina, 88040-900 Florianópolis, SC, Brazil. Fax: +55 48 3721 6850.
E-mail address: welz@qmc.ufsc.br (B. Welz).

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In recent years Cu, Mo and Sb were identified as traffic-related elements (TRE), as up to 4% of Cu, 1% of MoS_2 and 7% of Sb_2S_3 are used in brake linings (or pads) [1]. Kukutschová et al. [2] estimated that approximately 30,000 tonnes of break wear debris is being released in the USA yearly and investigated the mutagenic potency and pulmonary toxicity of wear debris. Several studies were carried out recently to assess the influence of traffic on atmospheric pollution in urban areas and to determine TRE in urban aerosols [1,3]. Several investigations were carried out on the determination of Sb as a new global pollutant in APM [4–6]. In a comprehensive study, Weckwerth [7] analyzed APM by neutron activation analysis in samples collected at 12 sites in Cologne (Germany); he compared the measured levels with specific element patterns from relevant emission sources such as coal, soot, tires, brake linings, and rails. On the basis of the agreement between the Cu and Sb ratio (~5) in brake linings and measured levels in APM, it was suggested that both elements might be taken as quantitative tracers for the brake-lining component in APM. In 67 samples of APM collected in Buenos Aires (Argentina) Sb concentrations varied between 0.9 and 15.3 ng m^{-3} with a mean value of 4.7 ng m^{-3} [4]. The Cu:Sb ratio was calculated to further support the view that brake linings contribute significantly to the aerosol fraction <10 μm (PM-10), and values between 5.6 and 8.0 were determined [8].

APM is often collected on glass-fiber filters using high-volume samplers with a PM-10 filter, and a typical sampling flow rate of 1000 L min^{-1}. However, the determination of trace elements in APM collected on glass fiber filters is difficult because of the refractory nature of the matrix. The total analyte concentration can only be determined after acid digestion in the presence of hydrofluoric acid, a procedure that is relatively time-consuming and certainly not without problems. Digestions in hydrofluoric acid are dangerous, and next to silicon, which should be removed in this manner, a number of elements, including Sb, form volatile fluorides which might be lost during sample preparation. Owing to these problems, instead of a total digestion, it is common in environmental analysis to use leaching with *aqua regia* [4,8–10]. This method, however, should be considered an acid leaching rather than a digestion, which cannot replace a determination of the total content of an analyte in all situations. In addition, the resulting acid matrix can cause serious interferences in most spectrometric techniques, such as ICP-MS or GF AAS. This means that the solutions need to be strongly diluted, which is often not possible in trace element determinations, or the analyte has to be extracted, which is another time-consuming procedure. The determination of Cu, Mo, Sb and other trace elements in APM with direct solid sampling (SS) GF AAS appears as an attractive alternative [11–14]. Even though, it still presents problems when conventional line-source GF AAS is used because complex matrices may cause spectral interference due to molecular absorption with rotational fine structure, such as that caused by SiO [15]. High-resolution continuum source AAS (HR-CS AAS), in contrast, offers much more sophisticated and efficient background correction [15,16]; background that is continuous within the spectral range covered by the array detector is corrected automatically and simultaneously using correction pixels on both sides of the analytical line, whereas structured background can be corrected using reference spectra and a least-squares algorithm [14–17].

The aim of this study has been to develop a fast, reliable and sensitive alternative to conventional methods for Cu, Mo and Sb determination in APM, collected on glass fiber filters, using direct solid sampling HR-CS GF AAS, and hence avoiding the dissolution of the sample. The proposed procedure will be compared with conventional techniques with respect to accuracy (agreement) of the results, precision, limits of detection and quantification, and the time necessary to carry out a complete analysis, a factor that is of importance for routine analysis.

Table 1
Temperature program for the determination of Cu, Mo and Sb in APM collected on glass fiber filters; argon gas flow rate 2.0 L min^{-1} in all stages except during atomization, where the gas flow rate was turned off.

Stage	Temperature (°C)	Ramp (°C s^{-1})	Hold time (s)
Drying	110	5	10
Pyrolysis	1100[a], 1200[b], 900[c]	300	15
Atomization	2100[a], 2550[b], 1800[c]	3000	5[a,c], 8[b]
Cleaning	2500[a,c], 2650[b]	500	4

[a] Cu.
[b] Mo.
[c] Sb.

2. Experimental

2.1. Instrumentation

All measurements were carried out using a contrAA 700 high-resolution continuum source atomic absorption spectrometer (Analytik Jena AG, Jena, Germany) with a flame and a transversely heated graphite tube atomizer in two separate sample compartments. The instrument is equipped with a 300 W xenon short-arc lamp, operating in a hot-spot mode, as continuous radiation source for the wavelength range from 185 to 900 nm, a high-resolution double monochromator, consisting of a prism pre-monochromator and an echelle grating monochromator, providing a spectral bandwidth per pixel of about 1.6 pm at 200 nm, and a linear charge coupled device (CCD) array detector with 588 pixels, 200 of which are used for analytical purposes, displaying the vicinity of the analytical line at high resolution.

The main absorption line at 324.754 nm or the secondary line at 216.509 nm was used for the determination of Cu, depending on the analyte content in the samples. The primary absorption line at 313.259 nm was used for Mo and the secondary line at 212.739 nm for Sb determination. All measurements were made with 300 scans per reading, with an integration time of 10 ms each.

The graphite furnace technique was used exclusively for all measurements. A manual solid sampling system SSA 6 (Analytik Jena), consisting of a rail and a pre-adjusted pair of tweezers to introduce the solid sampling platforms (Analytik Jena Part No. 407-152.023) into the solid sampling graphite tubes without a dosing hole (Analytik Jena Part No. 407-A81.303) were used for direct solid sampling. The samples were weighed on an M2P micro balance (Sartorius, Göttingen, Germany) directly onto the SS platforms. Pyrolytically coated graphite tubes with integrated PIN platform (Analytik Jena Part No. 407-A81.025) and an MPE 60 autosampler were used for the comparative measurements with partly digested samples, using a sample volume of 10 μL. The integrated absorbance of three pixels has been added (peak volume selected absorbance, PVSA, $A_{\Sigma 3,\mathrm{int}}$) [18], resulting in the best signal-to-noise ratio. Argon 99.996% (Oxilar, Florianópolis, Brazil) was used as purge and protective gas. The temperature program used for the determination of the three elements is shown in Table 1.

For comparison, one of the filter samples was also subject to a microwave-assisted acid leaching using a TOPwave laboratory microwave oven (Analytik Jena) with contact-free temperature and pressure control in each of the eight digestion vessels. The same filter sample was also subject to an ultrasound-assisted extraction using an Ultrasonik 28x NDI bath (Ultrasonik, NEY, Inc., Bloomfield, CT, USA).

2.2. Reagents and standards

All reagents used in this work were at least of analytical grade. Nitric acid (Merck, Darmstadt, Germany) was further purified by double sub-boiling distillation in a quartz still (Kürner

Table 2
Temperature program for the partial digestion of the filter sample with *aqua regia* in a microwave oven.

Parameter	Value
Temperature (°C)	175
Pressure (bar)	40
Power (%)	90
Ramp (min)	1
Time (min)	10

Analysentechnik, Rosenhein, Germany). Distilled and deionized water obtained from a Model Mega ROUP Mega Purity System (Equisul, Pelotas, Brazil) with a specific resistivity of 18 MΩ cm was used throughout for sample dilution and preparation of calibration solutions. All bottles were decontaminated with 30% (v/v) nitric acid for 24 h and then rinsed with deionized water three times before use.

The standards used were prepared by serial dilution of the stock solution with water. Copper and molybdenum standards were prepared from 1000 mg L^{-1} stock solutions (Merck, Darmstadt, Germany); the antimony stock solution (1269 mg L^{-1} in 2 mol L^{-1} HCl) was prepared from Sb_2O_3 (SPEX, Edison, NJ, USA). For the determination of antimony, Ru has been used as a permanent modifier. A stock solution containing 1000 mg L^{-1} Ru (Fluka, Buchs, Switzerland) has been used as provided for coating of the platform. Ten repetitive injections of 40 μL of the stock solution, each one followed by a five-step temperature program with previously optimized ramp and hold times [15], have been used for coating the platform with a total of 400 μg of Ru modifier.

The certified references materials (CRM) BCR 176R, “Fly Ash” (European Commission, Community Bureau of Reference, Brussels, Belgium), NIST 1648, “Urban Particulate Matter” and NIST 1649a, “Urban Dust” (National Institute for Standards and Technology, NIST, Gaithersburg, MD, USA), were used for validation purposes.

2.3. Samples and sample preparation

Airborne particulate matter was collected in different places of Buenos Aires, Argentina, on ash-free glass-fiber filters using a high-volume air sampler (SIBATA, HV 1000F, Japan) with a PM-10 sampling head. The sampling flow rate was 1000 L min^{-1} and the average total sampling time was 24 h, resulting in an average air volume filtered during 24 h of 1440 m^3. Details of the sampling procedure and the treatment of the filters loaded with APM have been described in earlier work of our group [6].

Once in the laboratory, filters loaded with airborne particulate matter and blank filters were heated in a drying oven at 50–60 °C for 120 min, the border without particulate matter was cut off and the remaining filter with APM was cut into eight pieces of similar size to investigate the homogeneity of the deposition; all pieces were weighed accurately for further calculation. The sub-pieces were ground manually in an agate mortar and kept in closed polyethylene tubes until analysis. Six glass fiber filters, denominated LDC-5, LDC-6, LDC-7, LDC-8, S-36 and S-54 were analyzed in this study.

For comparison, one of the filter samples was partially digested with *aqua regia* in a laboratory microwave oven. About 200 mg of ground filter material was weighed accurately into the PTFE vessels of the microwave digestion system; 12 mL of *aqua regia* was added, the vessels were closed, inserted into the microwave oven, and the program shown in Table 2 was executed. After that the vessels were allowed to cool down for about 30 min and opened carefully. The content of each vessel was diluted to 15 mL with water before the analysis. All digestions were carried out in triplicate, and a blank digestion of an unused filter was carried out in each run.

For the ultrasound-assisted extraction about 100 mg of filter material was weighed accurately into 15-mL plastic tubes and 12 mL of *aqua regia* was added. The mixture was left in the ultrasonic bath at room temperature for 1 h. After that the extract was diluted to 15 mL with water and the extract decanted from the filter residues before the analysis; all experiments were carried out in triplicate, and a blank extraction of an unused filter was carried out in each run.

3. Results and discussion

3.1. Optimization of instrumental parameters

3.1.1. Pyrolysis and atomization curves

The pyrolysis and atomization curves for the three analytes, using an aqueous standard solution, a solution of the filter LDC-6 in *aqua regia* after partial microwave-assisted digestion, and the same filter using direct solid sampling and a sample mass of approximately 0.2 mg are shown in Fig. 1a–c. For copper (Fig. 1a) the pyrolysis and atomization curves under the three conditions were essentially identical, indicating that there was no matrix effect, neither from the *aqua regia* nor from the filter matrix, and there was no need to use any modifier. For molybdenum (Fig. 1b) the pyrolysis and atomization curves for the filter sample using direct solid sampling and the microwave-assisted extraction were essentially identical, showing that there is no matrix effect whatsoever. The pyrolysis and atomization curves for the aqueous standard were also very similar, except for the different analyte concentration in the standard and the sample. No modifier was necessary for the determination of molybdenum; the maximum pyrolysis temperature was 1200 °C and the optimum atomization temperature was 2550 °C. For antimony (Fig. 1c) the conditions established in a previous work of our group for direct solid sampling analysis [6] have been adopted, and both, the solid sampling platform and the platform for liquid analysis have been coated with 400 μg Ru as a permanent modifier. Although the sensitivity for direct solid sampling appears to be slightly lower than for the *aqua regia* extraction, this difference becomes marginal at the optimum pyrolysis temperature of 900 °C and an atomization temperature of 1800 °C. The behavior of the aqueous standard was very similar to that of the sample, solid or extracted, which again indicates that there is essentially no matrix influence on the signal of antimony.

3.1.2. Selection of wavelengths

For the determination of copper the primary wavelength at 324.754 nm was selected for method development and for the determination of low concentrations of copper. The absorbance spectrum over time in the vicinity of this line is shown in Fig. 2a, and it is obvious that no spectral interference can be seen at this wavelength. For the higher copper concentrations in the filters LDC, however, it was necessary to reduce the sensitivity of the determination in order to be able to introduce a sufficiently large sample mass into the furnace when direct solid sampling was used. For this reason the secondary line at 216.509 nm was used, which is about one order of magnitude less sensitive than the primary line. Some structured background appeared in the vicinity of this line, as well as an atomic absorption line of nickel at 216.636 nm, as can be seen in Fig. 2b. However, neither the background nor the nickel absorption was overlapping with the analyte line, so that no additional measures had to be taken to correct for these spectral events.

The primary resonance line at 313.259 nm was used exclusively for the determination of molybdenum, and the aqueous standard exhibited an ideal signal shape under the atomization conditions used here, as is shown in Fig. 3a. When a filter sample was analyzed, the analyte signal still showed a perfectly symmetric shape, as shown in Fig. 3b; the only other thing that appeared was again a nickel absorption line, which, however, did not cause any kind

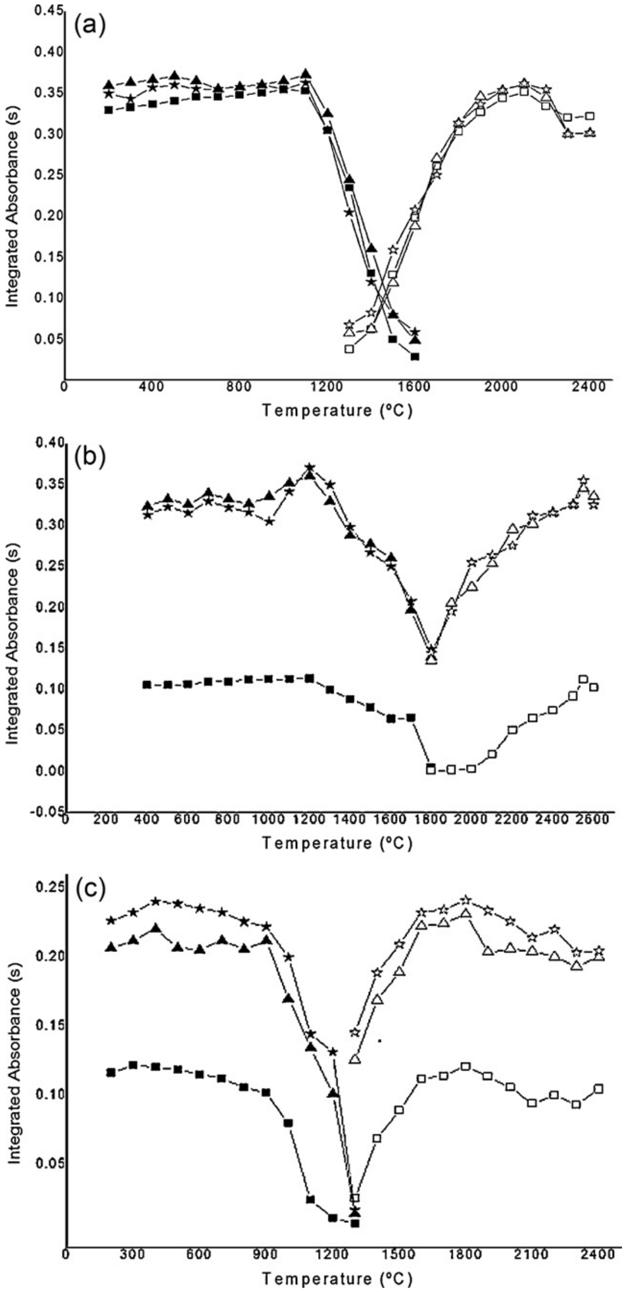

Fig. 1. Pyrolysis and atomization curves for (a) copper, (b) molybdenum and (c) antimony under the different conditions used in this work; full symbols: pyrolysis curves; open symbols: atomization curves; ■, □: 20 μL of aqueous standard solution containing 25 μg L^{-1} of the analyte; ▲, △: filter LDC-6, direct solid sampling; ★, ☆: filter LDC-6 extracted in *aqua regia*.

of interference, and might even be used for a simultaneous determination of these two elements. Although nickel is obviously of environmental importance, its determination was not considered in this study, as it is not a typical component of brake pads, the contribution of which to contamination has been the main topic of this investigation.

3.2. Comparison of sample preparation procedures

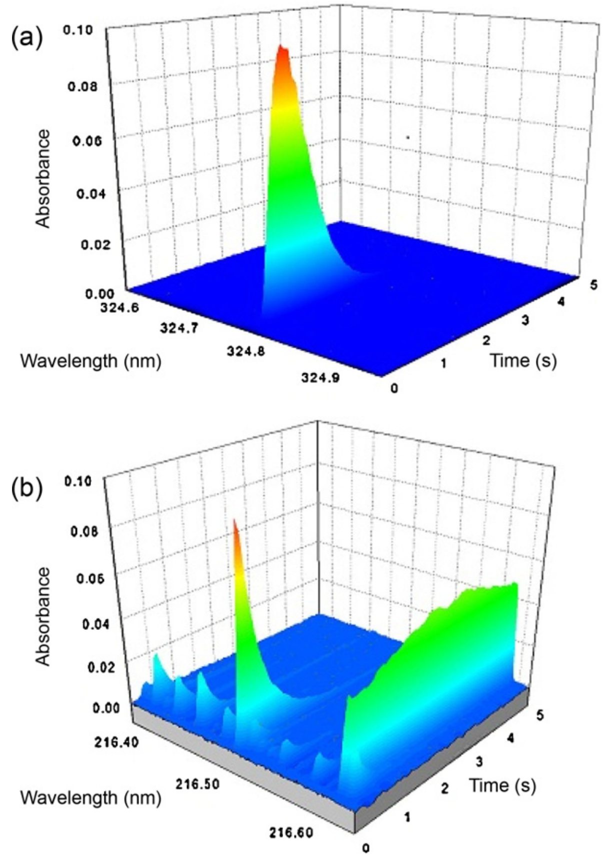

Fig. 2. Time- and wavelength-resolved absorbance spectra for copper in APM collected on glass fiber filters: (a) in the vicinity of the primary line at 324.754 nm and (b) in the vicinity of the secondary line at 216.509 nm.

For comparison, the filter "LDC-6" has been chosen to be analyzed after a partial microwave-assisted digestion and after ultrasound-assisted leaching using *aqua regia* in both cases, and using the same instrumental parameters as for direct solid sampling. The results are shown in Table 3; there is no significant difference between the results for copper and antimony obtained with the three methods based on a Student *t*-test on a 95% confidence interval. The result obtained for molybdenum using the ultrasound-assisted leaching might be considered slightly low, depending on the statistical program used; however, the difference is not very big. The precision obtained with the three procedures is also very similar and typically between 5 and 10% RSD. The results show that a partial microwave-assisted digestion without the use of hydrofluoric acid is sufficient to extract the investigated analytes from the particulate matter.

Another comparison between the three sampling and sample preparation techniques is shown in Table 4, where the limits of detection (LOD) and quantification (LOQ) are compared for the three analytes. The LOD is defined as three times the standard deviation of 10 measurements of a blank, divided by the slope of the calibration curve; the LOQ is based on 10 times the standard deviation of the same measurements. The best LOD and LOQ have been obtained using the solid sampling technique; however, the values obtained for the two extraction techniques are very similar, so that this criterion cannot be used to choose between the three

Table 3
Results obtained for the determination of copper, molybdenum and antimony in the glass fiber filter LDC-6 with direct solid sampling, after microwave-assisted partial digestion and after ultrasound-assisted leaching; all values in μg g^{-1}.

Method	Cu	Mo	Sb
Solid sampling	714 ± 43	179 ± 9	238 ± 19
Microwave	705 ± 50	167 ± 5	235 ± 20
Ultrasound	680 ± 70	150 ± 10	230 ± 10

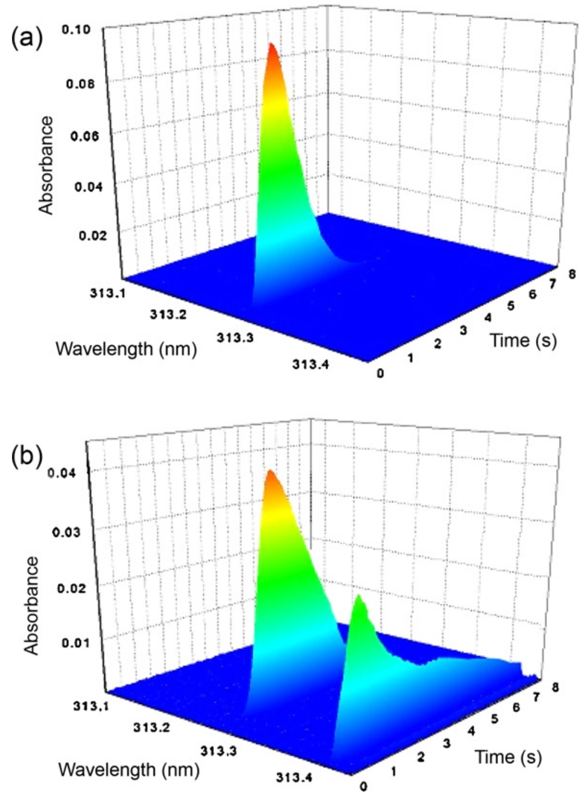

Fig. 3. Time- and wavelength-resolved absorbance spectra for molybdenum in the vicinity of the primary line at 313.259 nm: (a) aqueous standard solution and (b) in APM collected on a glass fiber filter using direct solid sampling.

techniques. There are at least two reasons for that similarity of the results: firstly, the blank measurements for solid sampling were made inserting and "atomizing" ca. 0.2 mg of an unused filter into the graphite furnace, which has been shown to deteriorate the LOD significantly, compared to inserting an empty SS platform [6]; in contrast to this, although the acid extract of an unused filter has been used for the other two techniques, this extract contained no detectable concentration of the investigated analytes, and the filter matrix was not introduced into the atomizer. Secondly, very concentrated extract solutions have been used in these experiments, so that the total amount of sample or sample extract introduced into the furnace tube was very similar for all three techniques.

A third comparison has been made considering the total analysis time and the reagents used for each of the three methods. The initial sample preparation, i.e., the grinding of the filters, is the same for all three procedures, which means that it does not count. The same is true for the calibration, which uses aqueous calibration solutions in all three cases, i.e., there is no difference either. The final determination, which is typically carried out in triplicate, is largely determined by the graphite furnace temperature program, and takes about 10 min in the present case for liquid sampling and 13 min for solid sampling, which is not a significant difference. The only significant difference is in the additional sample preparation for the extraction techniques, which takes at least 60 min for the microwave-assisted partial extraction, including sample weighing, introduction into the microwave oven, cooling and diluting the samples. The same procedure takes about 90 min in the case of the ultrasound-assisted acid leaching procedure. In addition, with both procedures an almost concentrated *aqua regia* extract is introduced into the graphite tube, which results in rapid deterioration of the graphite parts; any dilution of the acid obviously would result in a proportional deterioration of the LOD and LOQ.

Table 4
Limits of detection (LOD) and limits of quantification (LOQ) for copper, molybdenum and antimony in glass fiber filters using direct solid sampling, after microwave-assisted partial digestion and after ultrasound-assisted leaching; all values in $\mu g\,g^{-1}$.

Analyte	Solid sampling		Microwave extract		Ultrasound leaching	
	LOD	LOQ	LOD	LOQ	LOD	LOQ
Cu	15	50	15	50	18	60
Mo	15	50	18	60	21	70
Sb	15	50	18	60	21	70

Table 5
Results obtained for the determination of copper in two filter samples, S-36 and S-54, each one divided into eight parts in order to test homogeneity, using direct solid sampling HR-CS GF AAS and calibration with aqueous standard; $\lambda = 324.754$ nm.

Section no.	Cu in filter S-36 ($\mu g\,g^{-1}$)	RSD (%)	Cu in filter S-54 ($\mu g\,g^{-1}$)	RSD (%)
1	120 ± 6	5	90 ± 5	6
2	123 ± 5	4	93 ± 5	5
3	122 ± 6	5	92 ± 5	5
4	121 ± 5	4	90 ± 6	6
5	120 ± 7	6	97 ± 8	8
6	127 ± 10	8	93 ± 7	7
7	124 ± 6	5	92 ± 5	5
8	122 ± 5	4	90 ± 5	6

For these reasons direct solid sampling analysis has been chosen as the better approach for the analysis of APM on glass fiber filters for our further investigations.

3.3. *Results obtained with direct solid sampling*

3.3.1. *Homogeneity tests*

One of the questions that arises when direct solid sampling is used instead of partial digestion or leaching techniques is about the homogeneity of the analyte distribution on the filter, as only small portions of the filter are used for a determination. For this reason, two filters, S-36 and S-54 were divided into eight parts to test the homogeneity. The results are present in Table 5; there was no significant difference in the copper content found in the different parts of the two filters at a 95% confidence interval, i.e., the analyte distribution over the filter can be considered homogeneous within experimental error. Neither antimony nor molybdenum could be detected in these filters; however, it might be assumed that their distribution shows comparable homogeneity, at least when they come from the same source of contamination, i.e., TRE.

3.3.2. *Validation of the method*

Three certified reference materials (CRM), BCR 176R (City Waste Incineration Ash), NIST SRM 1648 (Urban Particulate Matter) and NIST SRM 1649a (Urban Dust) have been analyzed, and the results are shown in Table 6. Unfortunately only one of the CRM had a

Table 6
Determination of Cu, Mo and Sb in three CRM: BCR 176R (City Waste Incineration Ash), NIST SRM 1648 (Urban Particulate Matter) and NIST SRM 1649a (Urban Dust) using direct solid sampling HR-CS GF AAS and calibration against aqueous standard solutions; all values in $\mu g\,g^{-1}$; all found values are average ± standard deviation of $n = 5$ determinations.

CRM	Analyte	Certified	Found
BCR 176R	Cu	1050 ± 70	950 ± 70
	Sb	418 ± 18	430 ± 18
NIST SRM 1648	Cu	609 ± 27	615 ± 30
	Sb	45	50 ± 5
NIST SRM 1649a	Cu	223 ± 7	230 ± 8
	Mo	13.5 ± 0.9	15 ± 1
	Sb	29.9 ± 0.7	35 ± 5

Table 7
Results obtained for the determination of copper in the filters LDC, the air particulate matter (APM) and the atmospheric air, using direct solid sampling HR-CS GF AAS and calibration with aqueous standards; λ = 216.509 nm; all values are average ± standard deviation of $n = 5$ determinations.

Sample	Cu on the filter ($\mu g\,g^{-1}$)	Cu in APM ($mg\,g^{-1}$)	Cu in air ($ng\,m^{-3}$)	RSD (%)
LDC-5	680 ± 55	20.4 ± 1.6	2010 ± 161	8
LDC-6	714 ± 64	28.5 ± 2.5	2820 ± 254	9
LDC-7	758 ± 30	30.1 ± 1.2	2980 ± 119	4
LDC-8	832 ± 66	48.9 ± 3.9	4860 ± 389	8

Table 8
Results obtained for the determination of molybdenum in the filters LDC, the air particulate matter APM and the atmospheric air, using direct solid sampling HR-CS GF AAS and calibration with aqueous standards; all values are average ± standard deviation of $n = 5$ determinations.

Sample	Mo in the filter ($\mu g\,g^{-1}$)	Mo in APM ($mg\,g^{-1}$)	Mo in air ($ng\,m^{-3}$)	RSD (%)
LDC-5	163 ± 8	4.8 ± 0.2	498 ± 25	5
LDC-6	179 ± 9	7.5 ± 0.4	715 ± 36	5
LDC-7	193 ± 13	7.1 ± 0.5	762 ± 53	7
LDC-8	210 ± 17	12.3 ± 1.0	1215 ± 97	8

certified value for molybdenum; however, all the found values were in agreement with the certified ones at a 95% confidence interval. This shows that direct solid sampling HR-CS GF AAS with calibration against aqueous standards can be used for this kind of analysis.

The linear regression equations for the calibration of the three analytes were: copper: $A_{int} = 0.0053m_{Cu} + 0.0010$ ($R = 0.9999$); molybdenum: $A_{int} = 0.0126m_{Mo} + 0.0002$ ($R = 0.9985$); antimony: $A_{int} = 0.0037m_{Sb} + 0.0041$ ($R = 0.9995$).

3.3.3. *Results*

The results obtained for copper and molybdenum in the filters LDC-5 to LDC-8, in the collected APM and in the atmospheric air are shown in Tables 7 and 8, respectively. The values found for antimony in the same filters were already reported in an earlier publication [6]. The results for the determination of copper in the filters S-36 and S-54 have already been shown in Table 5 and are not repeated here; neither molybdenum nor antimony could be detected in these two filters. The precision, expressed as RSD, was better than 10% in all cases, which is quite acceptable for a routine determination of trace elements in APM collected on glass fiber filters.

All the results obtained in this and in previous work of our group [6] for copper, molybdenum and antimony in filter samples are compiled in Table 9. It is quite obvious that the ratio between the three analytes is very similar in the four filters LDC-5 to LDC-8, and comes close to a ratio of Cu:Mo:Sb ≈ 4:1:1.4 in all four samples, which suggests that the source of the three elements is the same. The limited number of samples analyzed in this study, which was more dedicated to method development, certainly does not allow any statistical evaluation; however, a comparison of our results with values published by others might be of some interest. Kukutschová et al. [2] investigated a semi-metallic brake lining pad that is widely used in the USA, in Europe and in Asia, which had a ratio of Cu:Mo:Sb ≈ 6.5:1:1.8 and a ratio of Cu:Sb ≈ 3.6, which is reasonably close to the ratios found in this work. Nevertheless these authors admit that there is a wide variety of brake materials in the market, and their actual compositions are most likely trade secrets. This composition might also change from country to country and with time, as new compositions might be introduced without announcing the change in public.

Table 9
Results obtained for the determination of copper, molybdenum and antimony in the glass fiber filters and their ratios using direct solid sampling HR-CS GF AAS and calibration with aqueous standards.

Sample	Cu in filter ($\mu g\,g^{-1}$)	Mo in filter ($\mu g\,g^{-1}$)	Sb in filter[b] ($\mu g\,g^{-1}$)	Cu:Sb	Cu:Mo	Sb:Mo
LDC-5	680 ± 20	163 ± 8	220 ± 13	3.1	4.2	1.3
LDC-6	714 ± 43	179 ± 9	238 ± 19	3.0	4.0	1.3
LDC-7	758 ± 30	193 ± 13	246 ± 10	3.1	3.9	1.3
LDC-8	832 ± 50	210 ± 17	342 ± 15	2.5	3.9	1.6
S-36	93 ± 10[a]	<15[a]	< 15[a]	–	–	–
S-54	125 ± 10[a]	<15[a]	< 15[a]	–	–	–

[a] Mean values taken from Table 5.
[b] Values taken from Ref. [6].

Most of the other authors did not include molybdenum in their studies, but reported a Cu:Sb ratio for APM collected in areas of intense traffic. Weckwerth [7] reported a ratio Cu:Sb ≈ 5 for samples collected at 12 sites in Cologne/Germany, whereas Voutsa et al. [19] reported Cu:Sb ratio between 13.2 and 17.4 for samples from the urban area of Thessaloniki/Greece. Gómez et al. [8] found Cu:Sb ratio between 5.6 and 8.0 for a large number of samples collected in Buenos Aires/Argentina and concluded that this ratio indicates that the source of the pollution is due to brake linings. We might therefore assume, based on the ratio between the determined elements that the source of contamination found in the LDC filters is due to brake linings as well, i.e., traffic related. In contrast to that, the copper contamination found on the filters S-36 and S-54 might be of different origin, as no molybdenum and antimony could be detected on these filters.

4. Conclusions

A simple, fast and reliable procedure for the determination of copper, molybdenum and antimony in airborne particulate matter collected on glass fiber filters has been developed using direct solid sampling and high resolution continuum source graphite furnace atomic absorption spectrometry. The results were in agreement with those obtained after microwave-assisted acid digestion, and – except for molybdenum – also with ultrasound-assisted acid leaching. A clear advantage of direct solid sampling is that the method does not require any toxic or corrosive acids and does not produce any hazardous waste; in addition the method is fast, as it does not require any sample preparation except of grinding the filters. Calibration could be carried out against aqueous standards, which further simplifies the procedure. It might be expected that other trace elements, collected with APM on glass fiber filters, could be determined using the same or a similar procedure.

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