Determination of antimony in airborne particulate matter collected on filters using direct solid sampling and high-resolution continuum source graphite furnace atomic absorption spectrometry

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A method has been developed for the determination of antimony in airborne particulate matter collected on glass fiber filters using direct solid sampling and high-resolution continuum source graphite furnace atomic absorption spectrometry. The certified reference material, BCR 176 (City Waste Incineration Ash) has been analyzed for validation purposes; no statistically significant difference has been found between the certified and the determined value for antimony based on a Student t-test at a 95% confidence level. The secondary antimony absorption line at 212.739 nm, which is about a factor of 20 less sensitive than the primary resonance line, has been used in order to adapt the sensitivity of the method to the antimony concentration in the samples. 400 µg of ruthenium, thermally deposited on the solid sampling platform has been used as permanent modifier. The characteristic mass at this line was found to be $m_0 = 0.7$ ng Sb. The limit of detection (3σ), based on ten atomizations of an unused filter was found to be 15 µg g^{-1}, corresponding to 40 ng m^{-3} for a typical air volume of 1440 m³. The limits of quantification, based on the same measurements were 50 µg g^{-1} and 128 ng m^{-3}, respectively. The repeatability of the measurements has been between 4% and 9% ($n = 5$). The antimony concentration found in filter samples varied between <15 µg g^{-1} and 342 ± 16 µg g^{-1}, corresponding to <40 ng m^{-3} and 1820 ± 90 ng m^{-3}, respectively. Direct solid sample analysis and detection by high-resolution continuum source graphite furnace atomic absorption spectrometry proved to be a simple, fast and reliable alternative for the determination of Sb in airborne particulate matter. An attempt to transfer the method to conventional line source equipment has been without success because of spectral interference and the weak emission of the secondary line from a hollow cathode lamp.

1. Introduction

Antimony is a potentially toxic trace element that may produce adverse effects to humans and the environment and has no known physiological functions. Fossil fuel combustion, non-ferrous metals refining, waste and sewage sludge incineration represent the major anthropogenic input of this metalloid into the environment.[1] The US Environmental Protection Agency (EPA) lists Sb and its compounds as principal pollutants.[2] The Occupational Safety and Health Administration (OSHA) of the United States Department of Labor has set an occupational exposure limit of 0.5 mg m^{-3} for Sb and its compounds in air for an 8-hour working day, 40-hour working week.[3]

In recent years Sb was identified as traffic related element (TRE), as up to 7% of Sb (as Sb_2S_3) are used in brake linings as lubricant to reduce vibrations and to improve friction stability. 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.[4,5] In a comprehensive study, Weckwerth[6] analyzed airborne particulate matter (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/Sb ratios (~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 another study, samples from the urban area of Thessaloniki (Greece) were analyzed;[7] antimony concentrations varied from 0.4 to 30 ng m^{-3}. It was found that Cu/Sb ratios ranged between 13.2 and 17.4. In 67 samples of APM collected in Buenos Aires (Argentina) Sb concentrations varied between 0.9 to 15.3 ng m^{-3} with a mean value of 4.7 ng m^{-3}.[8] The Cu/Sb ratios were calculated to further support the view that brake

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linings contribute significantly to the aerosol fraction <10 μm (PM-10), and values between 5.6 and 8.0 were determined.[9] Samples were collected on glass-fiber filters, acid digested and Sb was determined by inductively coupled plasma mass spectrometry (ICP-MS).

The determination of trace elements in APM collected on glass fiber filters is particularly 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 antimony, 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*.[4,9–11] 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 matrix can cause serious interferences in most spectrometric techniques, such as ICP-MS or graphite furnace atomic absorption spectrometry (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 Sb and other trace elements in APM with direct solid sampling (SS) GF AAS appears as an attractive alternative.[12–14] 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.[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; structured background can be corrected using reference spectra and a least-squares algorithm.[15,16]

The aim of this study has been to develop a fast, reliable and sensitive alternative to conventional methods for Sb determination in APM, collected on glass fiber filters, avoiding the dissolution of the sample. As all analytical lines are available with the same high intensity in HR-CS AAS, part of the investigation has been to select the absorption line that would cover best the concentration range of Sb in APM, making possible a determination in the optimum working range, and the use of a reasonable sample size to be introduced into the graphite tube. It has also been investigated if the method optimized with HR-CS GF AAS could be transferred to conventional line source AAS equipment.

2. Experimental

2.1. Instrumentation

All experiments have been carried out with a prototype high-resolution continuum source atomic absorption spectrometer, built at ISAS Berlin, which is based on a Model AAS 6 Vario (Analytik Jena AG, Jena, Germany), from which the entire optical compartment, including detector and associated controls, had been removed and replaced by a double monochromator, similar to the system described by Becker-Ross *et al.*[17] The spectrometer consists of a pre-dispersing prism and an echelle grating monochromator, both in Littrow mounting, resulting in a spectral resolution of $\lambda/\lambda\Delta \approx 140\,000$. A xenon short-arc lamp XBO 301 (GLE, Berlin, Germany) with a nominal power of 300 W operating in *hot-spot* mode is used as the continuum radiation source. The detector is a UV-sensitive charge coupled device (CCD) array, 200 pixels of which are used for analytical purposes, which corresponds to a spectral environment of about ±0.16 nm around the analytical line at 212.739 nm that becomes visible. The system is controlled by a personal computer with software developed at ISAS; details of this equipment have been described elsewhere.[16,18]

Atomic absorption has been measured using peak volume selected absorbance (PVSA),[19] *i.e.*, the integrated absorbance summated over three pixels ($A_{\Sigma3,\,int}$) around the line core, corresponding to a spectral interval of ~5 pm, as the best signal-to-noise (S/N) ratio has been obtained under these conditions.

The conventional transversely heated graphite tube atomizer system supplied by Analytik Jena together with the Model AAS 6 Vario has been used throughout. All experiments were carried out using pyrolytically coated SS graphite tubes without dosing hole (Analytik Jena, Part No. 407-A81.303). Samples were weighed onto SS platforms (Analytik Jena, Part No. 407-152.023) using an M2P micro-balance (Sartorius, Göttingen, Germany, accuracy: 0.001 mg), and inserted into the graphite tubes using a pre-adjusted pair of tweezers, which is part of the SSA 5 manual SS accessory (Analytik Jena). Argon 99.996% (White Martins, São Paulo, Brazil) has been used as the purge and protective gas. The temperature program adopted for aqueous standards (calibration) and for solid samples is shown in Table 1.

Some comparative measurements have also been carried out using a conventional line source atomic absorption spectrometer Model AAS 5 EA (Analytik Jena AG, Jena, Germany), equipped with deuterium lamp background correction and an antimony hollow cathode lamp (Narva, Berlin, Germany), operated at a current of 7 mA. The transversely heated graphite tube atomizer of this equipment is identical in design with that of the prototype HR-CS GF AAS, and the same graphite parts have been used throughout.

The filter samples have been ground in a Vibratory Micro-Mill "pulviresette 0" (Fritsch GmbH, Idar-Oberstein, Germany). During the grinding stage liquid nitrogen has been used to

Table 1 Graphite furnace temperature program for the determination of Sb in airborne particulate matter collected on glass fiber filters by solid sampling HR-CS GF AAS using 400 μg Ru as permanent modifier. Purge gas (argon) flow rate 2 L min⁻¹ in all stages, except during atomization, where the gas flow has been interrupted

Program stage	T/°C	Ramp/°C s⁻¹	Hold time/s
Drying	90	5	10
Drying	130	7	10
Pyrolysis	900	100	15
Atomization[a]	1900	3000	5
Cleaning	2500	1000	5

[a] Reading in this stage.

facilitate the operation and to reach the desired granulometry. A Shimadzu (Kyoto, Japan) Superscan SS-550 scanning electron microscope has been used to investigate the filter material after it had been ground.

2.2. Reagents

Analytical grade reagents have been used throughout. The 65% HNO_3 (Merck, Germany) used to prepare aqueous calibration standards was further purified by sub-boiling distillation in a quartz apparatus (Kürner Analysentechnik, Rosenheim, Germany). Distilled, deionized water with a resistivity of 18 MΩ cm from a Milli-Q water purification system (Millipore, Bedford, MA, USA) was used for the preparation of aqueous calibration standards. Antimony stock solution (1269 mg L^{-1} in 2 mol L^{-1} HCl) was prepared from Sb_2O_3 (SPEX, Edison, NJ, USA). The working standards were prepared by serial dilution of the stock solution. Stock solutions containing 1000 mg L^{-1} Ru, Ir and W, respectively, (Fluka, Buchs, Switzerland) have been used as provided for coating of the platform with permanent modifiers. Ten repetitive injections of 40 μL of the 1000 mg L^{-1} stock solutions, 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 modifier.

All containers and glassware were soaked in 3 mol L^{-1} HNO_3 for at least 24 h and rinsed three times with deionized water before use.

The BCR 176 certified reference material (CRM) City Waste Incineration Ash (European Commission, Community Bureau of Reference, Brussels, Belgium) has been used for method validation. Five glass fiber filters, denominated LDC-5, LDC-6, LDC-7, LDC-8 and S-36 with APM collected at various sites of Buenos Aires, Argentina, with different traffic patterns have been analyzed in this study. No attempt has been made to correlate the values to the traffic density because of the insufficient number of filters that have been available in this study.

2.3. Procedure

For the determination of Sb in filter samples aliquots between about 0.05 and 0.2 mg were weighed directly onto the SS platforms and inserted into the graphite tube with the SSA 5 accessory. The CRM has been weighed and inserted in the same way. Calibration solutions were deposited manually (20 μL) onto the SS platforms using a micropipette with disposable tips.

2.4. Samples and sample preparation

Airborne particulate matter has been collected on ash-free glass-fiber filters (8 × 10 inch, average weight: 4.80 ± 0.02 g, ADVANTEC, GB100R, 0.6 μm nominal rating) 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 (typically from noon to noon of the next day) to achieve a mass of APM sufficient for trace element determination. The average air volume filtered during 24 h was 1440 m³. Each filter was placed in a clean polyethylene bag during transport and storage. The glass-fiber filters were heated in a vacuum drying oven at 110–120 °C for 120 min prior to use. The filters were weighed (after moisture equilibration) before

and after sampling to determine the net mass of APM collected. Filter conditioning environment during the 24-hour equilibration period included controlled temperature within less than ±3 °C and constant relative humidity within ±5%.

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 (average weight; 1.05 ± 0.03 g) and the remaining filter with APM was cut into eight pieces of similar size to investigate the homogeneity of the deposition; all pieces have been weighed accurately for further calculation. The sub-pieces have been ground in a cryogenic mill and kept in closed polyethylene tubes until analysis. The amount of APM collected on the filters investigated in this work was between 51.3 mg and 136.9 mg.

3. Results and discussion

3.1. SEM investigations

The particles generated after grinding have been investigated using scanning electron microscopy (SEM). Although the filter had been ground to very small needles, the material agglomerated to balls with a typical diameter between 100 and 200 μm, as shown in Fig. 1a. This formation of secondary agglomerates has been independent of the grinding time, and could also be observed when the filters were ground manually in an agate mortar. Obviously, this agglomeration made any sieving after the grinding process impossible. As only a very small number of particles with a shape different from the filter material could be observed outside the agglomerates, it might be assumed that most of the APM is actually contained within the agglomerates, which obviously contributes to homogeneity and representative sampling. From Fig. 1b, which shows these agglomerates at high magnification, it actually appears as if the APM were firmly attached to the glass fiber needles; this is an ideal situation for direct SS, as the risk of loss of APM due to segregation or sedimentation of smaller particles would be minimum. In a study of uniformity of elements deposited on glass fiber filters after collection of APM using a high-volume sampler, Marrero et al.[20] also observed a homogeneous deposition pattern for almost all elements determined in their study.

3.2. Optimization of SS-HR-CS GF AAS conditions

All method development and optimization experiments have been carried out using an aqueous standard solution and one
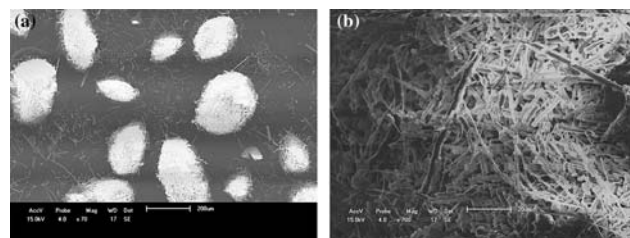

Fig. 1 Scanning electron micrographs of a glass fiber filter loaded with airborne particulate matter (APM) after grinding; (a) magnification 70×; (b) magnification 700×.

filter sample (LDC-8), which contained 136.9 mg of APM deposited on its surface.

The use of a modifier is typically required for the determination of Sb by GF AAS because of its volatility and the occurrence of double peaks in the absence of a modifier.[21] Palladium or a mixture of palladium and magnesium nitrates are the modifiers used most frequently for Sb.[21] However, as the manual addition of a modifier in solution over the solid sample on the SS platform complicates the process, only permanent modifiers thermally deposited onto the platform surface have been investigated in this study. Iridium, ruthenium and tungsten, which have been applied as kind of a surface coating on the platforms, have been tested. Without a modifier first analyte losses from an aqueous solution started at 800 °C, but no analyte has been lost from the filter sample up to 1000 °C. Tungsten did not only have no stabilizing power at all, but caused losses of Sb at lower pyrolysis temperatures than without a modifier. This clearly indicates some interaction of antimony with the graphite, which is prevented by the tungsten layer. The best sensitivity has been obtained with the iridium modifier, but the highest thermal stability of Sb has been provided by the ruthenium permanent modifier, so that the latter one has been chosen for our further experiments. A pyrolysis temperature of 900 °C and an atomization temperature of 1900 °C have been employed for the determination of Sb by SS-HR-CS GF AAS in APM collected on the glass fiber filters. Some structured background absorption could be observed under these conditions for the filter sample; however, there was no overlap between these structures and the analytical line, so that no special measures had to be taken to correct for this background.

3.3. Analytical line and figures of merit

It has been found in preliminary experiments that the concentration of Sb in the filter samples and/or the sensitivity of SS-HR-CS GF AAS were too high for a determination at the primary resonance line of Sb at 217.581 nm. The extremely small sample mass (less than 0.01 mg) that would have been necessary in this case to come within the normal working range would undoubtedly have had a negative effect on the precision of the procedure. Alternate lines have therefore been investigated, and the line at 212.739 nm, which is about a factor of 20 less sensitive than the primary line, has finally been chosen, as it made it possible to introduce a sample mass of 0.1–0.2 mg in order to get within the optimum working range.

The limit of detection (LOD) is usually calculated as three times the standard deviation of a blank, divided by the slope of the calibration curve; the limit of quantification (LOQ) is based on the same measurements, using 10 times the standard deviation of the blank readings. Unused filters that did not contain any APM have been used as blank to determine LOD and LOQ, and the results are shown in Table 2. LOD and LOQ were calculated both, for Sb on the filter material, based on the introduction of 0.2 mg of filter, and for Sb in the sampled air, based on a 24 h sampling interval, *i.e.*, 1440 m³ of air and 0.14 g of APM collected on the filter. It has to be stressed that these measurements have been carried out on a secondary line, and could be improved by at least one order of magnitude if necessary using the main resonance line of Sb.

Table 2 Figures of merit for the determination of Sb in airborne particulate matter collected on glass fiber filter using SS-HR-CS GF AAS and Ru as the permanent modifier. Values were calculated for Sb on the filter, based on a filter mass of 0.2 mg, and for Sb in the air, based on an air volume of 1440 m³

Parameter	Sb on filter	Sb in air
LOD (3σ)	15 μg g^{-1}	40 ng m^{-3}
LOQ (10σ)	50 μg g^{-1}	128 ng m^{-3}

The characteristic mass (m_0) is defined as the mass of the analyte that produces a PVSA of 0.0044 s. The characteristic mass obtained for Sb at the 212.739 nm line was 0.7 ng; no literature data could be found for this secondary Sb line for comparison. A calibration curve established using a blank and six calibration solutions in the concentration range 0.5–2.5 mg L^{-1} Sb (range mass: 10–50 ng Sb) in 0.007 mol L^{-1} HNO$_3$, using the conditions described in the Experimental part gave the linear relationship: $A_{\Sigma3, \text{int}} = 6.43 \ 10^{-3} \ m_{\text{Sb}} + 0.00205$ ($R = 0.9997$), where m_{Sb} is the analyte mass. This demonstrates the high sensitivity of the method that can be attributed mainly to the absence of any dilution with the SS technique.

3.4. Accuracy and precision

The accuracy of the proposed method has been confirmed analyzing the CRM City Waste Incineration Ash (BCR 176). A value of 430 ± 18 μg g^{-1} Sb has been found ($n = 5$), which is not statistically different compared to the certified value of 418 ± 18 μg g^{-1} Sb, based on a Student t-test at a confidence level of 95% ($t_{\text{calculated}} = 1.917$; $t_{\text{value}} = 2.776$, $n = 5$). The precision expressed as relative standard deviation (RSD%, $n = 5$) was better than 4% for the determination of Sb in the CRM.

The influence of the filter mass (loaded with APM) that was introduced into the furnace on the signal measured for antimony is shown in Fig. 2; a linear correlation between the PSVA and the sample mass has been obtained in the range from 0.061–0.170 mg with a correlation coefficient R > 0.99. Each measurement point in Fig. 2 corresponds to an individual sample weighing and measurement, reflecting directly the repeatability of the whole procedure.
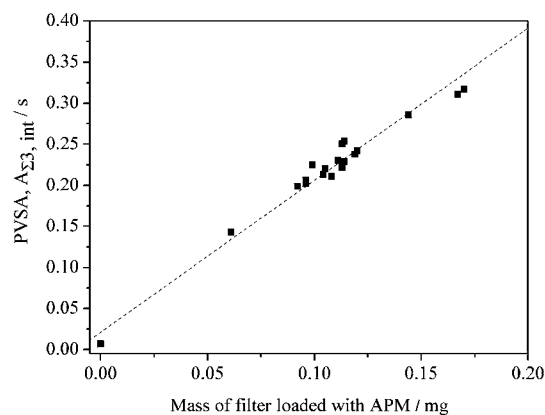

Fig. 2 Correlation between the LCD-8 filter mass (including the deposited APM) introduced into the graphite furnace and the PVSA ($A_{\Sigma3, \text{int}}$); $R = 0.99$; $T_{\text{pyr}} = 1200$ °C; $T_{\text{at}} = 2100$ °C; 400 μg Ru as permanent modifier.

Table 3 Results obtained for the determination of antimony on the glass fiber filter, in the airborne particulate matter (APM) and in the air, using direct solid sampling HR-CS GF AAS and calibration against aqueous standards with Ru as permanent modifier; $n = 5$

Sample	Sb on filter/ μg g⁻¹	Sb in APM/ mg g⁻¹	Sb in air/ ng m⁻³	RSD/%
LDC-5	220 ± 13	6.5 ± 0.5	620 ± 40	6
LDC-6	238 ± 19	9.9 ± 0.9	920 ± 80	8
LDC-7	246 ± 10	9.2 ± 0.4	820 ± 40	4
LDC-8	342 ± 16	20.4 ± 0.9	1820 ± 90	9
S-36	<15	<0.38	<40	—

3.5. Analytical results for airborne particulate matter collected on filters

The proposed method has been applied for the determination of antimony in five filter samples loaded with masses between 51.3 mg and 136.9 mg of APM, collected in the urban area of Buenos Aires, Argentina. The antimony content found in these filter samples, calculated for the loaded filter material, for the APM that has been collected, and per m³ of air, is shown in Table 3. The Sb concentrations found in this work are, except for one filter, significantly higher than those reported by other authors. Particularly the content of Sb in the APM collected on the filters has been found to be up to 2% w/w, which means that the collected material must have been to a significant extent due to brake linings. The concentration of Sb found in the air of Buenos Aires was between <40 ng m⁻³ and 1820 ± 90 ng m⁻³, which is also much higher than previously reported values; however, these differences might be due to climatic influences or a different traffic situation. The precision, expressed as relative standard deviation (RSD, $n = 5$), ranged between 4% and 9%, which is also an indication that the antimony is quite homogeneously distributed within the ground filter material.

3.6. Experiments with line source AAS

Because the determination with HR-CS GF AAS has essentially been without problems, an attempt has been made to transfer the method to a conventional line source instrument that was equipped with the same type of graphite tube atomizer. First experiments were carried out at the primary Sb resonance line at 217.6 nm; however, as expected, the high analyte content in the samples did not allow making any reasonable measurements. An attempt to use the 212.7 nm secondary line, which has been used in HR-CS AAS, have been equally unsuccessful, as the intensity of the line emitted by the hollow cathode lamp was very weak, resulting in excessive noise. In addition there appeared to be some spectral interference, most likely due to the SiO molecular spectrum, when the filter samples were atomized. No additional attempt has been made to search for other secondary Sb lines in order to make this determination possible.

4. Conclusions

A simple, fast and reliable procedure for the determination of 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. A clear advantage 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. The advantage of using HR-CS GF AAS and its capability do deal with all kind of spectral interference has also been demonstrated, as it has been impossible to transfer the method to a conventional line-source spectrometer. It could also be expected that other trace elements, collected with APM on glass fiber filters, can be determined using the same or a similar procedure.

References

1 J. M. Pacyna and E. G. Pacyna, *Environ. Rev.*, 2001, **9**, 269.
2 http://www.epa.gov accessed on 03/08/2009.
3 http://www.osha.gov/dts/chemicalsampling/data/CH_219100.html accessed on 03/08/2009.
4 P. Smichowski, D. Gómez, C. Frazzoli and S. Caroli, *Appl. Spectrosc. Rev.*, 2008, **43**, 22.
5 S. Canepari, C. Perrino, F. Olivieria and M. L. Astolfi, *Atmos. Environ.*, 2008, **42**, 8161.
6 G. Weckwerth, *Atmos. Environ.*, 2001, **35**, 5525.
7 D. Voutsa, C. Sâmara, Th. Kouimtzis and K. Ochsenkühn, *Atmos. Environ.*, 2002, **36**, 4453.
8 P. Smichowski, D. R. Gómez, L. E. Dawidowski, M. F. Giné, A. C. Sánchez Bellato and S. L. Reich, *J. Environ. Monit.*, 2004, **6**, 286.
9 D. R. Gómez, M. F. Giné, A. C. Sánchez Bellato and P. Smichowski, *J. Environ. Monit.*, 2005, **7**, 1162.
10 S. Canepari, C. Perrino, M. L. Astolfi, M. Catrambone and D. Perret, *Talanta*, 2009, **77**, 1821.
11 X. Y. Zhang, L. S. Tang, G. Zhang and H. D. Wu, *Bull. Environ. Contam. Toxicol.*, 2009, **82**, 31.
12 U. Kurfürst, ed., *Solid sample analysis*, Springer, Berlin, 1998.
13 M. G. R. Vale, N. Oleszczuk and W. N. L. dos Santos, *Appl. Spectrosc. Rev.*, 2006, **41**, 377.
14 B. Welz, M. G. R. Vale, D. L. G. Borges and U. Heitmann, *Anal. Bioanal. Chem.*, 2007, **389**, 2085.
15 R. G. O. Araujo, B. Welz, F. Vignola and H. Becker-Ross, *Talanta*, 2009, **80**, 846.
16 B. Welz, H. Becker-Ross, S. Florek and U. Heitmann, *High-Resolution Continuum Source AAS*, Wiley-VCH, Weinheim, 2005.
17 H. Becker-Ross, S. Florek, U. Heitmann and R. Weisse, *Fresenius J. Anal. Chem.*, 1996, **355**, 300.
18 A. F. Silva, D. L. G. Borges, B. Welz, M. G. R. Vale, M. M. Silva, A. Klassen and U. Heitmann, *Spectrochim. Acta, Part B*, 2004, **59**, 841.
19 U. Heitmann, B. Welz, D. L. G. Borges and F. G. Lepri, *Spectrochim. Acta, Part B*, 2007, **62**, 1222.
20 J. Marrero, R. Jiménez Rebagliati, D. Gómez and P. Smichowski, *Talanta*, 2005, **68**, 442.
21 B. Welz and M. Sperling, *Atomic Absorption Spectrometry*, Wiley-VCH, Weinheim, 1999.