



Analytical Note

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

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ABSTRACT

A study has been undertaken to assess the capability of high-resolution continuum source graphite furnace atomic absorption spectrometry for the determination of mercury in airborne particulate matter (APM) collected on glass fiber filters using direct solid sampling. The main Hg absorption line at 253.652 nm was used for all determinations. The certified reference material NIST SRM 1648 (Urban Particulate Matter) was used to check the accuracy of the method, and good agreement was obtained between published and determined values. The characteristic mass was 22 pg Hg. The limit of detection (3σ), based on ten atomizations of an unexposed filter, was 40 ng g⁻¹, corresponding to 0.12 ng m⁻³ in the air for a typical air volume of 1440 m³ collected within 24 h. The limit of quantification was 150 ng g⁻¹, equivalent to 0.41 ng m⁻³ in the air. The repeatability of measurements was better than 17% RSD (n=5). Mercury concentrations found in filter samples loaded with APM collected in Buenos Aires, Argentina, were between <40 ng g⁻¹ and 381 ± 24 ng g⁻¹. These values correspond to a mercury concentration in the air between <0.12 ng m⁻³ and 1.47 ± 0.09 ng m⁻³. The proposed procedure was found to be simple, fast and reliable, and suitable as a screening procedure for the determination of mercury in APM samples.

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1. Introduction

Mercury occurs naturally in the environment in several inorganic and organic mercury compounds [1]. Mercury that is released into the environment will remain there for an indefinite period of time. The form of mercury (organic or inorganic) may change with time; some or all of the organic mercury may slowly be converted to inorganic mercury, and some of the inorganic mercury might be slowly transformed into organic mercury by bacteria in soil or water [2].

The US Environmental Protection Agency (EPA) [3] is an agency of the federal government, charged with protecting human health and the environment, including air, water, soil, and industrial studies, with laws and regulations on mercury and its compounds to protect the environment [4]. The Agency for Substances and Disease Registry

(ATSDR) sets the limit concentration of exposure for mercury and compounds per cubic meter of air [5]. In turn, the values obtained by ATSDR informed by the Occupational Safety and Health Administration of the United States Department of Labor has set an occupational exposure limit of 0.1 mg of mercury per cubic meter of air (mg m⁻³) for organic mercury and 0.05 mg m⁻³ for metallic mercury vapor in workplace air to protect workers during an 8-hour shift and a 40-hour week of work [6].

Mercury in airborne particulate matter (APM) originates from both natural (crustal, aquatic, etc.) and anthropogenic sources (smelters, fossil fuel combustion, waste incineration, etc.) [7,8]. It is estimated that one third to two thirds of the total Hg released annually comes from human activities. The levels of Hg in the atmosphere (i.e., in the air that we breathe) are very low and usually do not pose any health risk; however, the steady release of Hg has resulted in current levels that are three to six times higher than the estimated levels in the pre-industrial era atmosphere [1,2].

The average concentration of mercury in airborne particulate matter from urban and suburban sites in Beijing was reported as

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$1.18 \pm 0.82 \text{ ng m}^{-3}$ with a range of 0.18–3.51 ng m^{-3} at an urban site and $0.68 \pm 0.62 \text{ ng m}^{-3}$ with a range of 0.13–2.40 ng m^{-3} at a suburban site. These results indicate that anthropogenic sources in Beijing significantly contribute to mercury content in the air and subsequently to the mercury depositions, especially during coal burning in winter for heating [9].

Cold vapor atomic absorption spectrometry (CV AAS) is recognized as a routine procedure for mercury determination in various fields, due to the advantages of efficient matrix separation, high analyte transport efficiency, high selectivity, simple instrumentation and ease of automation. However, the presence of heavy metals in the matrix might cause interference in complex matrices and any kind of sample pre-treatment is a potential source of errors due to contamination and/or analyte loss [10].

Conventional high-volume samplers, which are frequently used for collecting APM, consist of a pre-filter that excludes particles $>10 \mu\text{m}$, and the APM is collected on a glass-fiber filter for 24 h. The filter is subsequently digested or extracted with an acid mixture, followed by spectrometric analysis [11–13]. The major disadvantage of the conventional technique is that it involves several sample handling steps, which require ultra-clean sampling techniques and a clean room facility to avoid contamination. This problem is particularly serious in the case of Hg determination; moreover, the time required for this process is usually quite long.

An attractive alternative for trace element determination in complex matrices might be the direct analysis without any sample preparation, using solid sampling graphite furnace AAS (SS-GF AAS), as has been proposed for the determination of mercury in environmental reference materials [14], in soils [15], in biological samples [16] and in polymers [17]. SS-GF AAS was also used for the determination of antimony in airborne particulate matter collected on glass fiber filters [18], although this cannot be directly compared due to the significantly different volatility of the analytes and the different wavelength range in which the analytes absorb, and hence the potential spectral interferences. This technique essentially requires only a minimum of sample preparation, represents a minimum risk of contamination, provides highest sensitivity as no dilution is involved, does not use chemicals, maybe except for a modifier, and requires less time due to the absence of sample preparation [19].

Nevertheless, SS-GF AAS might still encounter problems when volatile elements, such as Hg are determined and conventional spectrometers are employed, because complex matrices may cause spectral interferences [17]. To overcome this limitation, high-resolution continuum source AAS (HR-CS AAS) is a valuable tool due to its special features, which include visibility of the spectral environment at high resolution, automatic and simultaneous correction for continuous background and the possibility to correct for fine structured background by subtracting a reference spectrum [19,20]. All these features make SS-HR-CS GF AAS very attractive for routine application, as accurate results can be obtained very rapidly [16–19].

The aim of this study was to develop a fast, reliable and sensitive alternative to conventional methods for Hg determination in APM, avoiding sample dissolution. It has also been investigated if HR-CS GF AAS would allow direct solid sampling analysis of the filters, as this would obviously result in the highest sensitivity and shortest analysis time.

2. Experimental

2.1. Instrumentation

All experiments were carried out with a prototype high-resolution continuum source atomic absorption spectrometer, built at ISAS Berlin, based on an AAS 6 Vario atomic absorption spectrometer (Analytik Jena AG, Jena, Germany), from which the entire optical compartment, including detector and associated controls, was

removed and replaced by a double monochromator (DEMON), and a charge-coupled device (CCD) array detector, similar to the system described by Becker-Ross et al. [21]. A xenon short-arc lamp XBO 301 (GLE, Berlin, Germany) with a nominal power of 300 W operating in *hot-spot* mode was used as the continuum radiation source. The prototype equipment was described in detail in previous papers of our group [20,22,23]. Peak volume selected absorbance (PVSA) [24], i.e. the sum of the integrated absorbance measured at three pixels (center pixel ± 1), corresponding to a spectral interval of $\sim 6 \text{ nm}$, was used exclusively for signal evaluation, as the best signal-to-noise (S/N) ratio was obtained under these conditions.

All experiments were carried out using pyrolytically coated SS graphite tubes (Analytik Jena AG, Part no. 407-A81.303). Samples were weighed onto SS platforms (Analytik Jena AG, no. 407-152.023), using a M2P micro-balance (Sartorius, Göttingen, Germany), and inserted into the graphite tubes using a pre-adjusted pair of tweezers, which is part of the SSA 5 manual solid sampling accessory (Analytik Jena). Argon 99.996% (White Martins, São Paulo, Brazil) was used as purge and protective gas. The temperature program adopted for aqueous standards (calibration) and for solid samples is shown in Table 1.

2.2. Reagents

Analytical grade reagents were used throughout. The nitric acid 65% v/v (Merck, Germany), used to prepare aqueous calibration standards, was further purified by sub-boiling distillation in a quartz apparatus (Kürner Analysentechnik, Rosenheim, Germany). Water was de-ionized to a resistivity of 18.2 M Ω in a Milli-Q apparatus (Millipore, Bedford, MA, USA). All containers and glassware were soaked in 3 mol L $^{-1}$ nitric acid for at least 24 h and rinsed three times with deionized water before use. The stock standard solution for mercury (1000 mg L $^{-1}$) was prepared from high-purity Spex (Edison, NJ, USA) reagent PLK20-Hg (HgO), which was dissolved in 2% (v/v) nitric acid. The calibration solutions were prepared by serial dilution of the stock standard with 0.07 mol L $^{-1}$ nitric acid plus 0.10 mg of potassium permanganate (Merck, Darmstadt, Germany) to a final volume of 10 mL. The certified reference material (CRM) NIST SRM 1648 Urban Particulate Matter (National Institute for Standards and Technology, Gaithersburg, MD, USA) was used for validation of the method.

2.3. Samples and sample treatment

Four glass fiber filters with APM collected in Buenos Aires, Argentina, in 2001 were analyzed in this study. Airborne particulate matter was collected on ash-free glass-fiber filters (8 \times 10 in., 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) to accumulate a Hg concentration that was sufficient for its quantification. The average air volume collected was 1440 m 3 . Each filter was placed in a clean polyethylene bag during transport and storage. The glass-fiber filters were heated in a vacuum

Table 1

Graphite furnace temperature program for the determination of Hg in filter samples by SS-HR-CS GF AAS using 1% m/v KMnO $_4$ as chemical modifier.

Program stage*	Temperature/°C	Ramp/°C	Hold/s
Drying 1	60	10	1
Drying 2	100	10	10
Auto zero	100	100	1
Atomization	1300	1000	8
Cleaning	1700	2000	5

* Purge gas (argon) flow rate 2 L min $^{-1}$ in all stages, except during atomization, where the gas flow was interrupted for reading.

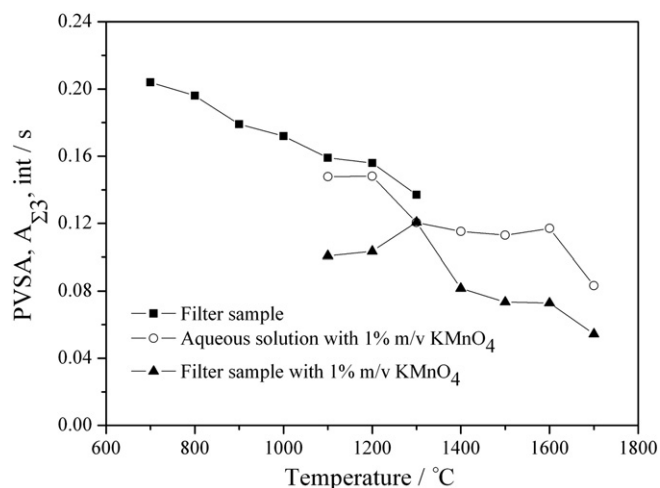


Fig. 1. Atomization curves for mercury in a filter sample without and with 1% m/v KMnO_4 as the modifier, and for an aqueous solution with 1% m/v KMnO_4 .

drying oven at 110–120 °C for 120 min prior to their use. The filters were weighed (after moisture equilibration) before and after sampling to determine the net particulate mass gain. Filter conditioning environment during the 24-hour equilibration period included controlled temperature with less than ± 3 °C and constant relative humidity within $\pm 5\%$.

Once in the laboratory, filters loaded with APM and blank filters were heated in a drying oven at 30–40 °C for 120 min prior to be ground in a cryogenic mill. The ground filter samples were stored in polyethylene tubes until they were analyzed. The shape and size of the particles generated in the grinding process were discussed in an earlier paper from our group [18]. The fine needles that had formed during grinding had agglomerated to balls with a typical diameter between 50 and 200 μm with only very little loose material in between. This phenomenon was independent of the way of grinding the filters; the same structures were also observed after manual grinding in an agate mortar. The formation of these agglomerates was actually an advantage for direct solid sampling, as it facilitated to a great extent the handling of the ground samples. Sample aliquots between 0.75 and 3.6 mg were weighed directly onto the SS platforms and inserted into the graphite tube with the SSA 5 accessory for the determination of Hg in filter samples. Calibration solutions (20 μL) and the modifier solution were injected manually onto the SS platforms.

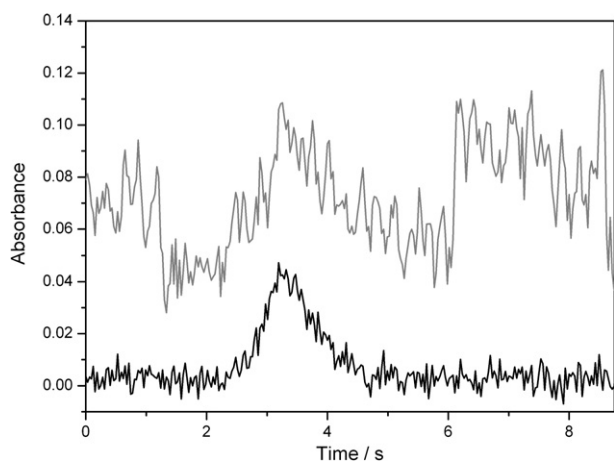


Fig. 2. Absorbance over time for Hg in 1.168 mg of filter LCD-6 with APM at the center pixel (253.652 nm) without (gray line) and with (black line) automatic correction for continuous events; atomization temperature 1300 °C.

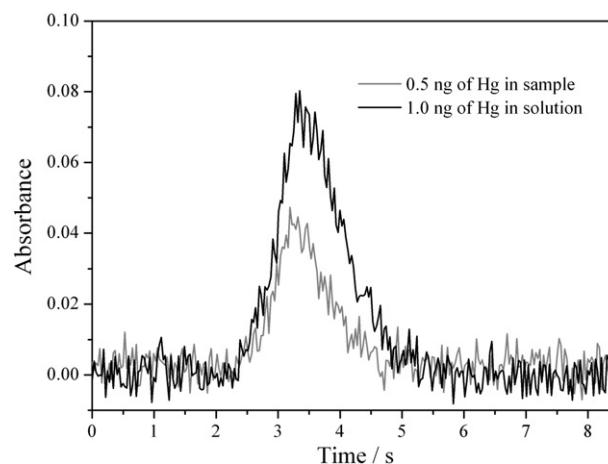


Fig. 3. Superimposed transient signals of Hg for the filter sample (gray signal) and for the aqueous standard solution (black signal) using an atomization temperature of 1300 °C.

3. Results and discussion

All method development and optimization have been carried out using filter LCD-6 with 0.0932 g of APM deposited on its surface. All calculations have taken into consideration the total mass of the filter and the mass of APM (glass-fiber filter + APM), respectively.

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

The use of a modifier is usually required for the determination of Hg by GF AAS because of the extremely high volatility of this element and its compounds, in order to avoid losses in the drying and pyrolysis stages. Silva et al. [14] investigated several permanent modifiers to stabilize mercury and found that it was necessary using a 3% (m/v) solution of KMnO_4 to stabilize Hg in the aqueous standards in order to avoid analyte losses already in the drying stage due to reduction at the graphite surface, which was confirmed by others in later work [15,16]. Other modifiers have been proposed in order to stabilize mercury in

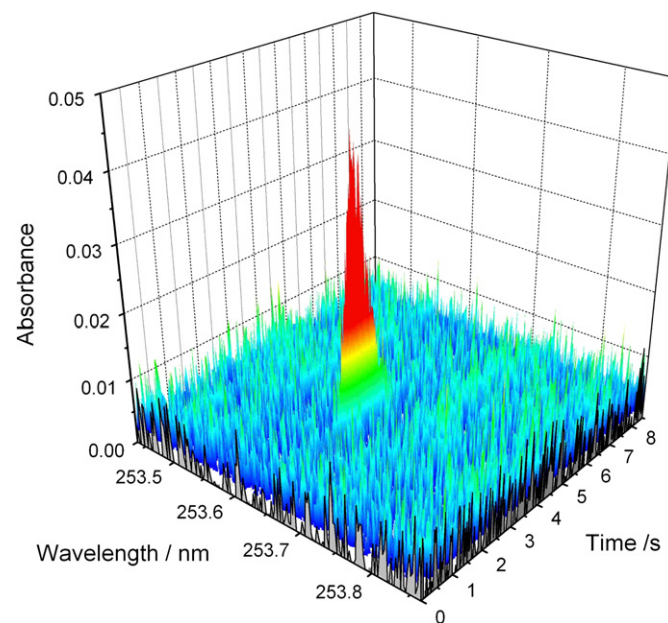


Fig. 4. Time- and wavelength-resolved absorbance spectrum for 1.160 mg filter LCD-6 with APM in the environment of the Hg line at 253.652 nm, using the temperature program given in Table 1.

Table 2

Figures of merit for the determination of Hg in airborne particulate matter collected on glass fiber filter using SS-HR-CS GF AAS and 1% m/v KMnO₄ as the chemical modifier. Values were calculated for Hg on the filter, based on a filter mass of 2.0 mg, and for Hg in the air, based on an air volume of 1440 m³.

Parameter	Hg on filter	Hg in APM	Hg in air
LOD (3σ)	40 ng g ⁻¹	1.3 μg g ⁻¹	0.12 ng m ⁻³
LOQ (10σ)	150 ng g ⁻¹	4.3 μg g ⁻¹	0.41 ng m ⁻³

different inorganic matrices using slurry sampling, such as silver nitrate [25] or palladium [26,27], both in combination with KMnO₄. In our investigations, the concentration of the KMnO₄ solution has been reduced to 1% (m/v), as this concentration was found to be sufficient to avoid analyte losses in the drying stage. No pyrolysis stage has been used in this work, as it could not be expected that any significant part of the SiO₂ matrix could be removed at a temperature that ensures that no analyte is lost. Fig. 1 shows the atomization curves for Hg in the filter material loaded with APM without and with the addition of KMnO₄, and for the aqueous standard only with the addition of KMnO₄. The atomization curves exhibit a pattern that is according to expectation as, particularly for volatile elements, the integrated absorbance, as a measure of the atom cloud density in the atomizer, decreases with increasing atomization temperature due to the increased diffusion losses. For the filter sample without a modifier, a very high integrated absorbance was obtained already at an atomization temperature of 700 °C; however, this is not very useful, as aqueous standards used for calibration need a modifier in order to avoid analyte losses. With increasing atomization temperature the integrated absorbance signal decreases almost linearly due to the above-described diffusion losses. At around 1300 °C the two curves, without and with modifier, coincide, and the curve for the aqueous standard also reaches the same value. This means that an atomization temperature of 1300 °C is ideal for this application, taking into consideration all the various aspects.

Considering the atomization curves for the filter sample with and without the addition of KMnO₄, it appears so, as if the addition of this stabilizer would not be necessary, as the two curves are essentially identical between 1100 °C and 1300 °C. This is most likely due to the fact that the mercury collected on the filter material does not come into contact with the graphite material in the drying stage, so that losses due to reduction to elemental mercury are unlikely. Nevertheless, this was not further investigated, and KMnO₄ was added to aqueous solutions and solid samples in all future experiments.

3.2. Correction for continuous background absorption

In HR-CS AAS, all “continuous spectral events” that affect all pixels to the same extent are corrected automatically by the software. As all pixels are read out simultaneously, the system functions as a truly simultaneous double beam system, in which lamp flicker noise, continuous background absorption and/or emission are corrected automatically. Fig. 2 shows the transient signals obtained for the filter sample LCD-6 without and with automatic background correction at the center pixel at 253.652 nm. The background is very low, and could be corrected without any problems, although no pyrolysis stage has been used. This is according to expectation for an atomization

temperature of 1300 °C, where most of the matrix remains in the graphite tube up to the cleaning stage.

Fig. 3 shows the overlaid transient signals for the aqueous standard solution and the filter sample using the adopted conditions, i.e., an atomization temperature of 1300 °C and 1% (m/v) KMnO₄. Very similar peak shapes were obtained in both media, indicating that calibration against aqueous standard solutions might be feasible. The time- and wavelength-resolved absorbance spectrum obtained for the filter LCD-6 with APM using the optimized conditions, which is shown in Fig. 4, also indicates a trouble-free determination. Only the atomic absorption signal for Hg at 253.652 nm appears, and there is no structured background visible that could cause any interference, which is according to expectation considering the low atomization temperature. This fact might indicate that the method could be transferred to conventional line-source AAS equipment without significant loss in performance, although this has not been investigated in the present work.

3.3. Figures of merit

Unused filters without deposited APM have been used as blank to determine the limits of detection (LOD) and quantification (LOQ) shown in Table 2. They were calculated both for Hg on the filter material, based on the introduction of 2.0 mg of filter, and for Hg 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.

The characteristic mass (m_0), defined as the mass of the analyte that produces a PVSA of 0.0044 s, was found to be 22 pg Hg. This is about a factor of four better than values published for line-source AAS using the Pd–Mg mixed modifier [28], but is in agreement with previous results obtained using HR-CS GF AAS and the 1% (m/v) KMnO₄ modifier [16]. A calibration curve established using a blank and seven calibration solutions in the concentration range 10–75 μg L⁻¹ Hg (mass range: 0.2–1.5 ng Hg) prepared in 0.07 mol L⁻¹ HNO₃ and 1% m/v KMnO₄, using the conditions described in the Experimental part gave the linear relationship: $A_{\Sigma 3, \text{int}} = 0.2038m_{\text{Hg}} + 0.01103$ ($R = 0.9996$), where m_{Hg} is the analyte (mercury) 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

In order to confirm the accuracy of the method, the certified reference material NIST SRM 1648 – Urban Particulate Matter was used. Unfortunately, this reference material has no information about the concentration of Hg. For this reason, values reported in the literature [29], using two independent techniques, were taken as a reference. As shown in Table 3, the results obtained in this work are in agreement with the reference values, indicating that there is no statistically significant difference between the results obtained with the proposed method and reference values based on a Student *t*-test at a 95% confidence level.

3.5. Analysis of APM collected on filters

The proposed method has been applied for the determination of Hg in four filter samples collected in the urban area of Buenos Aires, Argentina,

Table 3

Mercury determination in NIST SRM 1648 using SS-HR CS GF AAS and 1% m/v KMnO₄ as a modifier; comparison with reference values from the literature [29].

CRM	Reference value adopted/μg g ⁻¹	Found value/μg g ⁻¹	$t_{\text{calculated}}$ Value ^c	%RSD (n = 5)
NIST 1648	1.07 ± 0.1 ^a	1.16 ± 0.18	1.42	13
	1.02 ± 0.05 ^b		2.17	

^a Extraction/amalgamation/cold vapor atomic fluorescence spectrometry.

^b Neutron activation analysis.

^c $t_{\text{tabulated}}$ value = 2.776 (n = 5) at a 95% confidence level.

Table 4
Results obtained for the determination of Hg on the filters, in the collected APM and in the air using direct SS-HR-CS GF AAS and calibration against aqueous standards and 1% m/v KMnO₄ as the modifier.

Samples	APM on filter/ $\mu\text{g m}^{-3}$	Found value Hg on filter ^a / ng g^{-1}	Found value Hg in APM ^b / $\mu\text{g g}^{-1}$	Found value Hg in air ^c / ng m^{-3}
LDC-5	95.1	80 ± 14	2.3 ± 0.4	0.50 ± 0.06
LDC-6	92.9	381 ± 22	16.0 ± 1.0	1.47 ± 0.09
LDC-7	67.4	<40	<1.3	<0.12
LDC-8	44.0	96 ± 15	5.3 ± 0.6	0.44 ± 0.06

^a Average of five determinations ± confidence interval (at the 95% level).

^b Based on [(Hg mass found in filter)/(particulate matter mass deposited on filter)].

^c Based on [(concentration of Hg found in airborne particulate matter) × (mass of APM deposited on filter)]/air volume collected.

as shown in Table 4. The filters were loaded with masses between 0.0513 g and 0.1369 g of APM, and containing between 44.0 μg and 95.1 μg APM per cubic meter of air. The mercury content found in these filter samples with APM was between <40 ng g^{-1} and 381 ± 22 ng g^{-1} , corresponding to between <1.3 $\mu\text{g g}^{-1}$ and 16.0 ± 1.0 $\mu\text{g g}^{-1}$ Hg in the collected APM, and between <0.12 ng m^{-3} and 1.47 ± 0.09 ng m^{-3} Hg in the air, respectively.

4. Conclusion

A simple, fast and reliable procedure for the determination of mercury in APM collected on glass fiber filters has been developed using SS-HR-CS GF AAS and calibration against aqueous standards with 1% (m/v) KMnO₄ as the modifier. An advantage of the direct SS analysis appears to be that it can apparently be applied to materials of significantly different physical structure and matrix composition. Another advantage is the relatively high analytical frequency due to the significantly reduced sample treatment and the fast temperature program. As direct SS-HR-CS GF AAS with similar fast temperature programs has already been described for the determination of Hg in soil [15], biological materials [16] and in plastic materials [17], it might be assumed that the procedure could be extended to various other matrices with only minor modification. One of the big advantages of the direct solid sampling compared to slurry techniques is that no corrosive and toxic acids, such as hydrofluoric acid, are used, which are typically applied in slurry preparation [25,26].

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