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Speciation of arsenic in coarse and fine urban aerosols using sequential extraction combined with liquid chromatography and atomic fluorescence detection

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Abstract An analytical procedure for speciation of As in urban aerosol samples was developed. The aerosols were collected by sequential filtration through membrane filters. Part of each filter was investigated by INAA for the total amount of As. Another part of the filters was treated by a sequential extraction procedure to differentiate between water-extractable, phosphate-extractable and refractory chemical forms. Water-extractable forms were further differentiated into anionic As species by HPLC-HGAFS. Extractability of As into water exhibited a clear dependency on the aerosol size fraction (12% in coarse fraction and 50% in fine fraction). Dependency of the phosphate extractable As on the aerosol size fraction seems not to be significant (10–15% in both size fractions). The remaining amount, i.e., about 78% of the coarse As and about 40% of the fine As was considered to be refractory or environmentally immobile As. Water-extractable As forms could only be attributed to arsenate.

Introduction

Atmospheric As is contained totally within the troposphere, and more than 90% of it is in particulate form with a diameter smaller than or equal to 3.5 μm [1]. This segregation is the primary (physical) speciation, which has an important implication for the residence time, dry and wet deposition rate, dispersion and transportation of As in the at-

mosphere [2, 3]. If deposited, chemical species play the most important role in influencing the environment through toxicity, reactivity or stability and environmental mobility of different compounds [4]. The extent to which aerosols undergo solubilisation in water depends on how the element is partitioned among the various compounds. Surface-associated constituents are considered to be loosely held or environmentally mobile, while compounds associated in the matrix (e.g., with silicate structure) are much less mobile and are usually considered to be refractory [4]. It is, therefore, of basic importance that any speciation analysis designed allows separation of the constituents attached to the aerosol particles on the surface from those incorporated in the matrix.

Most studies determine total As concentrations in aerosols, either directly in solid material with instrumental methods [5, 6] or after acid digestion with conventional spectrometric techniques [7, 8]. Hlavay et al. [3] conducted research on the sequential leaching of several elements, including As, from aerosols with ammonium acetate, hydroxylamine hydrochloride-acetic acid and nitric acid-hydrofluoric acid, respectively. Hydrochloric acid leaching followed by pH-selective hydride generation – to differentiate between arsenite and arsenate – has been applied for speciation of As in aerosols collected in Los Angeles [9]. Data on As speciation related to aerosols may be subject to several uncertainties generated by *i*) species alteration during sampling, *ii*) sequential extraction and by the fact that the procedure is defined operationally, *iii*) by contamination problems associated with ultra-low levels of As, and *iv*) by the insensitivity of analytical methods to certain As species. In general, these uncertainties can be (partially) addressed by critical assessment of the procedures used.

The present paper reports a mild sequential extraction procedure utilised directly for on-filter collected size-fractionated aerosol samples based on solubility of As in water and phosphate solution.¹

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Further objectives of the study were to develop a high performance liquid chromatography-hydride generation-atomic fluorescence spectrometry (HPLC-HGAFS) method for further differentiation between water-extractable As forms and application of the methods developed to urban aerosols.

Experimental

Reagents and standards

The chemicals used were at least of analytical grade. Millipore (Milford, MA, USA) Milli-Q Plus (MQ) water (18.2 M Ω cm) was used for all solution preparations. As₂O₃ and As₂O₅ were purchased from Merck (Darmstadt, Germany) and monomethylarsonic acid (MMAA) and dimethylarsinic acid (DMAA) were gifts from K.J. Irgolic (Karl-Franzens University Graz, Austria). Stock solutions of the As compounds containing 1000 mg L⁻¹ As were prepared in water and kept at 4 °C. Dilution of the stock solutions with water yielded working solutions with As concentrations of 1–10 ng mL⁻¹; these solutions were prepared fresh daily.

Sample collection and storage

The size-fractionated aerosol samples were collected by Gent-type stacked filter units (SFUs) [10]. The device contains a pre-impaction stage (upper size inlet cut-off) and two membrane filters (Ø 47 mm) with pore sizes of 8 µm (Apiezon-coated) and 0.4 µm all placed in series. The separation of the aerosol particles into two size fractions is achieved by sequential filtration through the filters at a flow rate of 15–16 L min⁻¹. The aerosol particles are separated into a coarse (about 10–2 µm EAD) and a fine (< 2 µm EAD) size fraction. The sample collection was performed at two urban sites, e.g., within the Castle District Tunnel and at Széna Square, both located downtown in Budapest [11, 12]. The Tunnel is 350 m long, about 9 m wide and varies from 8 to 11 m in height. It comprises 2-lane traffic of passenger cars, light-duty vehicles and buses. The SFU samplers were set up in the tunnel about halfway within the Tunnel 1.5 m above the ground, and the collections were performed from 8 a.m. to 4 p.m. on 11 and 12 May 1998. The mean sampled volume was 5.6 m³ air (1.33 mg aerosols). At the Széna Square, the SFU sampler was set up at 4.5 m above the ground and daily aerosol samples were taken from 7 a.m. onward with planned and regular interruptions on 13 and 14 May 1998. The mean sampled volume was about 24 m³ air (0.35 mg aerosols). A field blank sample was also collected performing the same manipulations and operations as for real samples including even drawing air through it for about 1 min. Average values for the daily temperature, pressure and humidity during the sampling were 20 °C, 101.4 kPa and 64%, respectively. There was no precipitation during the sampling period. Four SFU sample pairs and one field blank pair were collected altogether and were stored in plastic petri dishes in a refrigerator at 4 °C. The filters were then cut into sections. For speciation analysis, three quarter sections were employed, and one quarter section was investigated by INAA (instrumental neutron activation analysis).

Determination of total amount of As on filters

The total amount of As was determined by INAA as part of a panoramic analysis developed for the SFU samples [12]. Arsenic data were obtained by using ⁷⁶As ($T_{1/2} = 1.097$ d, $E_{\gamma} = 559.1$ and 657.1 keV) as the analyte radionuclide. The filter sections were pressed to pellets of 7 mm diameter, sealed in high purity quartz ampoules (Suprasil AN), and were activated together with a high purity, 25 µm thick Zr foil and an Al-0.1% Au wire (IRMM-530) for 18 h in the Budapest Research Reactor with a subcadmium neu-

tron flux of 1.6×10^{13} cm⁻²s⁻¹ and a subcadmium-to-epithermal neutron flux ratio of 32. The surface of the quartz ampoules was cleaned in an etching bath after activation, and the samples were measured after about 2 and 5 days of decay time for 2 and 4 h, respectively. The γ -ray spectrometer consists of a HPGe detector (relative efficiency 13%, FWHM = 1.74 keV at 1332.5 keV), Canberra-made signal processing electronics including a Loss-Free Counting module with dual option, and an Accuspec-B data acquisition card (resolution 2 × 8k). All γ -ray spectra were evaluated by the Hypermet-PC computer program [13], and the analytical calculations were performed using the k_0 -standardization method [14]. The concentration data obtained from different measurements and γ energies were expressed in atmospheric concentration units (ng m⁻³) at standard temperature and pressure (STP, 273.15 K and 1013.2 kPa) and were averaged. The detection limits for As depend on the loading of the filters, and were about 0.051 and 0.028 ng m⁻³ STP in the coarse and fine size fractions, respectively, for samples with small aerosol mass. The atmospheric concentrations obtained by INAA are usually compared to results from particle-induced X-ray emission analysis, and agree within 6–10% with each other [15].

Extraction procedure

The sequential extraction procedure comprised the following two steps: 1) A three-quarter section of each filter was placed in a 7 mL Sterilin test tube (50 × Ø 12 mm), wetted with 100 µL of methanol, and 5 mL of MQ water was added. The Sterilin test tube was closed, placed in a 25 mL Sterilin test tube (93 × Ø 25 mm) filled with MQ water, and sonicated for 3 h at 20 °C. The water extract was filtered through a 0.45 µm membrane filter, frozen at -50 °C and freeze-dried. To the dry residue, which was an invisible quantity, 1.5 mL of MQ water was added, and the solution obtained was used for chromatographic separation within two hours to prevent losses due to adsorption. 2) The original filter subjected to extraction with water and the 0.45 µm membrane filter used for the filtration of the water extract were joined, and 5 mL of 0.1 mol L⁻¹ KH₂PO₄ (pH 6.0) was added for the second extraction. The same preparation procedure was then repeated as for the water extract.

Arsenic determination in extracts

Arsenic species in water extracts using HPLC-HGAFS [16,17]. For separation of the anionic As species, i.e., of arsenite, arsenate, MMAA and DMAA, an HPLC-pump (LKB Bromma, Sweden) was fitted with an anion exchange guard column (Alltech All-guard Adsorbosphere SAX 5 µm, 7.5 × Ø 4.6 mm). Aliquots were injected via a Rheodyne 7725i injector (Rheodyne, Inc.; Cotati, California, USA) with a 500 µL sample loop, and 10 mmol L⁻¹ KH₂PO₄ (pH 6.0) was used as a mobile phase at a flow rate of 1.2 mL min⁻¹. The separated As species were subjected to hydride generation with HCl (4.4 mol L⁻¹, 3 mL min⁻¹) and NaBH₄ (1.5% w/v in 0.05% w/v NaOH, 3 mL min⁻¹) in a PEEK mixing cross (Upchurch Scientific, USA) yielding hydrogen and volatile arsines. The gas-liquid mixture was delivered to a gas-liquid separator, and the arsines and hydrogen were swept from the mixture with a flow of argon (400 mL min⁻¹). Arsines entering the atomic fluorescence spectrometer (model Excalibur, PS Analytical, Orpington, UK) were dried in a Perma-Pure mini-dryer, and atomised in a hydrogen/air flame aligned in the lightpath of a boosted As hollow cathode lamp. The field blank (field blank filter and contributions of extraction, filtration, freeze-drying and dissolution steps) was 0.085 ± 0.008 ng arsenate per filter.

Total As in phosphate extracts using FI-HGAFS. Since the phosphate concentration in the extracts was too high for speciation analysis (coeluting compounds in the void volume), only the total phosphate-extractable As was determined. A flow-injection (FI) set-up [18], i.e., the same instrumental configuration as above with exclusion of the chromatographic column, was used. The carrier stream was MQ water with a flow rate of 2.0 mL min⁻¹. The field blank was 1.32 ± 0.19 ng total As per filter ($n = 6$). This field blank is

much higher than the one reported for water extracts what can be attributed to As impurities in phosphate.

Data handling. Atomic fluorescence signals were recorded with a strip chart recorder. The analytical results were based on measurement of peak heights. Arsenic species were quantified by external calibration in the concentration range from 1 to 10 ng mL⁻¹. The analytical results were corrected for the field blanks. Each solution was analysed twice and the analytical data obtained were averaged resulting in a relative uncertainty < 10%, and were expressed in atmospheric concentration units (ng m⁻³ STP).

Results and discussion

Optimisation of speciation procedure

A two-stage sequential extraction procedure was applied to distinguish between As associated with the surface of aerosols or environmentally mobile As (water-extractable), As which is more strongly bound but still available under more severe conditions (phosphate-extractable) and As associated with the matrix or refractory As (non-extractable in this set-up). Due to low atmospheric arsenic concentrations heavy constraints are placed on the sensitivity of the detector. Freeze-drying of extracts increases the As concentration in the solutions to be analysed. Further differentiation between water-extractable As forms using HPLC-HGAFS benefits from introduction of large aliquots of pre-concentrated water extract. Since the main As forms expected in aerosols are arsenite and arsenate [9], a low-resolution anion-exchange guard column is suitable for separation [19]. At the same time this offers possibilities to increase the injection volume for better sensitivity. An example of the separation of arsenite and arsenate on an anion-exchange guard column with a 500 µL-injection loop

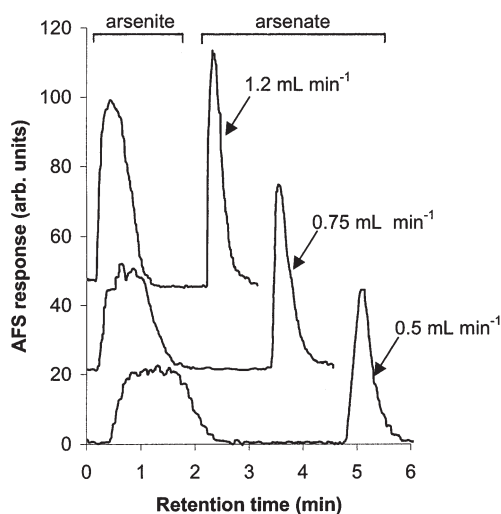


Fig. 1 Chromatograms obtained by separation of a mixture of arsenite (5 ng mL⁻¹) and arsenate (5 ng mL⁻¹) using mobile phase flow rates of 0.5, 0.75 and 1.2 mL min⁻¹; column, Alltech All-guard Adsorbosphere SAX 5 µm, 7.5 × Ø 4.6 mm; mobile phase, 10 mmol L⁻¹ KH₂PO₄, pH = 6.0; sample loop, 500 µL. For clarity the chromatograms for 0.75 and 1.2 mL min⁻¹ have been shifted in the vertical direction

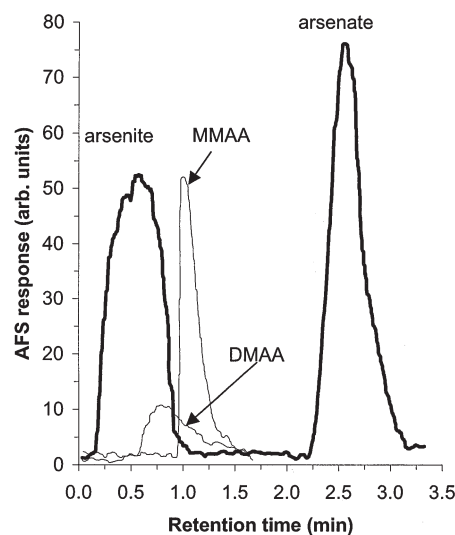


Fig. 2 HPLC-HG-AFS chromatogram showing where individual MMAA (2 ng mL⁻¹) and DMAA (5 ng mL⁻¹) peaks would be eluted in a mixture of arsenite (5 ng mL⁻¹) and arsenate (5 ng mL⁻¹); mobile phase flow rate 1.2 mL min⁻¹. For other conditions see Fig. 1

is depicted in Fig. 1. Since arsenite is not retained on the column, an arsenite peak with a plateau is observed at low flow rates due to a “continuous flow” of arsenite through the system. The arsenite peak get narrower and higher with increasing flow rate in accordance with the behaviour in a FI-HGAFS system [18]. From Fig. 2 it can be seen that MMAA may be base-line resolved as well in the same mixture whereas DMAA partially overlaps with the arsenite peak.

The As species mentioned were only determined in water extracts because high phosphate concentrations used in the extraction procedure interfere with the chromatographic separation resulting in coeluting peaks. The detection limits (3 · standard deviation of base-line noise of blank) were 0.12 ng mL⁻¹ for arsenite, 0.08 ng mL⁻¹ for arsenate, 0.04 ng mL⁻¹ for MMAA and 0.63 ng mL⁻¹ for DMAA.

Arsenic species may undergo alteration during sampling and/or sequential extraction. We found that arsenite undergoes partial oxidation (ca. 20%) during the extraction procedure when testing arsenite-containing water solutions with arsenite levels comparable to these expected in the water extracts from the aerosols. The other As species investigated were not altered by the extraction procedure. This implies that the results found for the aerosol extracts may be underestimated for their arsenite content and thus overestimated for their arsenate content. Additionally, results for aerosols may be influenced by the sampling procedure itself due to air filtration artefacts but this was not the subject of the present study.

Analysis of coarse and fine urban aerosols

The total absolute amounts, atmospheric concentrations and sequential extractability of As obtained for the coarse and fine aerosols collected at two urban sites in Budapest are

Table 1 Amount of As and its sequential extractability from coarse and fine aerosol fractions collected on membrane filters at two urban sites (Castle District Tunnel/Széna Square) in Budapest on two successive days (1/2)

Sampling site	Size fraction	Day	Sampled volume (m ³ STP)	As amount \pm st.d. (ng)	Atm. As conc. \pm st.d. (ng m ⁻³ STP)	As extractability (in % of total As)		
						water extractable ^a	phosphate extractable ^b	refractory ^c
CD Tunnel	coarse	1	4.80	17.9 \pm 1.2	3.7 \pm 0.3	11.0	13.6	75.4
		2	5.70	30.3 \pm 1.7	5.3 \pm 0.3	12.8	12.9	74.3
	fine	1	4.80	3.1 \pm 0.5	0.64 \pm 0.1	45.9	< 9.3	> 44.8
		2	5.70	< 1.7	< 0.30	> 40.0	> 16.7	< 43.3
Széna Sqr.	coarse	1	19.59	25.1 \pm 0.4	1.3 \pm 0.07	11.3	4.3	84.4
		2	25.23	15.4 \pm 0.8	0.61 \pm 0.07	12.3	9.8	77.9
	fine	1	19.59	50.8 \pm 0.4	2.6 \pm 0.08	58.7	12.4	28.9
		2	25.23	52.2 \pm 1.0	2.1 \pm 0.08	40.6	22.0	37.4

^a environmentally mobile

^b less mobile

^c non-extractable in procedure applied

Table 2 Speciation of As in water-extractable fraction of coarse and fine urban aerosols. For additional information see Table 1

Sampling site	Size fraction	Day	Concentration of As species (ng m ⁻³ STP)			
			As(III)	MMAA	DMAA	As(V)
CD Tunnel	coarse	1	< 0.11	< 0.04	< 0.58	0.41
		2	< 0.09	< 0.03	< 0.47	0.68
	fine	1	< 0.09	< 0.03	< 0.47	0.30
		2	< 0.05	< 0.02	< 0.26	0.12
Széna Sqr.	coarse	1	< 0.02	< 0.01	< 0.10	0.15
		2	< 0.01	< 0.01	< 0.05	0.08
	fine	1	< 0.02	< 0.01	< 0.10	1.52
		2	< 0.01	< 0.01	< 0.05	0.84

shown in Table 1. The absolute amounts of As determined by INAA range from < 1.7 to 52.2 ng, corresponding to atmospheric concentrations between < 0.30 and 5.31 ng m⁻³ STP.

The extractability of As into water exhibits a clear dependency on the aerosol size fraction, and it seems that the urban locations investigated have much less influence on it. Arsenic in the coarse size fractions was found to occur mainly as environmentally immobile forms as the water-extractable As was only about 12% of the total As. Since the sequential extraction indicates the real mobility of As species deposited, coarse As has only a limited impact on the urban environment. In contrast, the environmental mobility of the fine As is considerably higher; about half of the total As exhibited solubility in water. The phosphate-extractable As made up 10% of the total As for the coarse size fraction, and it was similar, about 15%, for the fine size fraction. Dependency of the phosphate extractable As on the aerosol size fraction seems not to be significant. As a consequence, the environmental impact of As seems to be dominated by fine As. The remaining As was non-extractable in the present extraction scheme leaving about 78% of the coarse size fraction and about 40% of the fine size fraction as refractory As. This agrees well with the results of an earlier study [3] on the moderately polluted city Tihany (Hungary) where 67% of As was associated with organic matter and silicates.

Table 2 shows that in all water extracts only arsenate was found, and none of the other anionic As species anticipated was detected by HPLC-HGAFS. The fact that in another study [9] the arsenite/arsenate ratios in HCl leachates from size-fractionated aerosols have been found close to 1 for both the fine and coarse size fractions suggests that arsenite in our samples could have been oxidised to arsenate in the air by oxidants such as ozone and/or on the filter during the sampling. This could also mean that arsenite released by most industrial processes is, in general, oxidised by the oxidative nature of the urban air to less toxic arsenate.

The analytical results obtained will be further used in the frame of an air pollution project to determine and interpret the chemical characteristics of the urban aerosol in Budapest.

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