Separation of microgram quantities of As(v), As(III) and organoarsenic species in aqueous solutions and determination by energy dispersive X-ray fluorescence spectrometry

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A procedure was developed for the separation and independent determination of microgram quantities of As(III), As(v), dimethylarsinic acid (DMAA) and phenylarsonic acid (PAS) in aqueous solution. The arsenic species were collected one by one from the same sample solution, by adsorbing them onto metal-loaded activated charcoal (MC*). PAS was separated by adsorption onto VC* and As(v) remaining in the filtrate was collected onto LaC*. The LaC* was filtered out and As(III) in the filtrate was separated by 1-pyrrolidinecarbodithioic acid, ammonium salt (APDC) coprecipitation, where Fe^{3+} acted as carrier and the precipitate was bound onto activated charcoal. Finally DMAA in the filtrate was collected onto ZrC*. Arsenic concentration in the metal-loaded activated charcoal was measured directly by energy dispersive X-ray fluorescence spectrometry (EDXRF). The detection limits for all four arsenic species were better than 0.02 mg L^{-1}. The amount of unadsorbed arsenic was determinated by vapour generation atomic absorption spectrometry (VGAAS) or graphite furnace atomic absorption spectrometry (GFAAS).

Introduction

Arsenic occurs in surface waters, soil pore water and ground water mainly as inorganic species, including arsenite and arsenate, and as methylated species, including monomethylarsonic acid (MMAA) and dimethylarsinic acid (DMAA).[1,2] Determination of the total amount of arsenic is not sufficient to assess the toxicity of a particular medium. The various chemical species exhibit widely differing levels of toxicity.[3] Inorganic arsenic exhibits high toxic levels, AsH_3 is very toxic, As(III) is more toxic than As(v), simple methylated species are less toxic and arsenobetaine and arsenocholine are not toxic at all.[2] Proper assessment of the toxicity of a medium requires that the various arsenic species be separated and directly determined.

Energy dispersive X-ray fluorescence spectrometry (EDXRF) allows easy and sensitive detection of a variety of pollutants in water and wastewater effluents. Among its advantages are simple sample preparation and the facility to determine many elements simultaneously. Because it is more convenient to use solid samples for EDXRF analysis, the ideal method of preconcentration results in a solid sample. A suitable preconcentration step will also eliminate or decrease the amount of interfering elements and provide the required elements in a homogeneous, solid, thin layer for XRF. The method needs to be rapid and simple, require minimum sample preparation and not contaminate the sample. Adsorption onto activated carbon (C*) is frequently the most efficient and economical method for removing impurities from water, particularly when the impurities are present in low concentration. Arsenic does not adsorb significantly onto C*, but the presence of active metal on the C* surface may greatly enhance the adsorption affinity. Metal-loaded activated charcoal (MC*) has been shown to be an advantageous collector material for EDXRF determinations.[4–6]

In this work we studied the effect on the adsorption of the various arsenic species when the activated charcoal surface was loaded with different metals. The metals tested as modifiers were Al, Cr(III), Fe, Hf, Mn, W, Ce, La, Ti, V, In and Zr. The adsorption conditions for each arsenic species on the most suitable MC* were optimized. The arsenic species were both inorganic [As(III) and As(v)] and organic species [dimethylarsinic acid (DMAA) and phenylarsonic acid (PAS)]. For the separation of As(III) from DMAA, we studied the coprecipitation of As(III) with 1-pyrrolidinecarbodithioic acid, ammonium salt (APDC), with Fe^{3+} acting as carrier, and subsequent adsorption onto activated charcoal.

This paper also describes a procedure by which As(v), As(III), DMAA and PAS concentrations can be determined independently in the same sample solution. The different arsenic species were collected from the sample solution one by one by adsorbing them onto metal-loaded activated charcoal (MC*). Arsenic concentration in the metal-loaded activated charcoal was then measured directly by EDXRF.

Experimental

Reagents and materials

A standard stock solution (1000 mg As L^{-1}) of As(III) was prepared by dissolving As_2O_3 (Merck 119, p.a., Darmstadt, Germany) in water. A standard stock solution (1000 mg As L^{-1}) of As(v) was prepared by diluting Titrisol standard As_2O_5 (Merck 9939) with water. Organoarsenic standard stock solutions (1000 mg As L^{-1}) were prepared by dissolving $(CH_3)_2AsNaO_2$ (Merck 527, p.a.) and $C_6H_5AsO(OH)_2$ (Merck 820670, p.a.) in 1 M HNO_3. Lanthanum nitrate ($La(NO_3)_3 \cdot 6H_2O$, Merck 5326, p.a.), vanadium(IV) oxide sulfate hydrate ($VOSO_4 \cdot 5H_2O$, Merck 8503, p.a.) and zirconyl nitrate hydrate ($ZrO(NO_3)_2 \cdot 1\frac{1}{2}H_2O$, Aldrich 24,349-3, p.a., Steinheim, Germany) were used for the preparation of the activated charcoal loaded with these metals. Charcoal activated powder (Merck 2186, p.a.) was used without further purification. 1-Pyrrolidinecarbodithioic acid, ammonium salt (APDC, Aldrich 14,269-7) was used to coprecipitate As(III). Iron(III) nitrate nonahydrate ($Fe(NO_3)_3 \cdot 9H_2O$, Riedel-de Haën 31233, Seelze, Germany) was used as the Fe^{3+} carrier. All reagents were analytical reagent grade, and water (Milli-Q Plus system) was ultrapure grade. The matrix modifier in graphite furnace

atomic absorption spectrometry (GFAAS) determinations was nickel solution made from standard stock solution (1000 mg Ni L^{-1}) by diluting Titrisol standard $NiCl_2$ (Merck 9989) with water. Polyethylene leaching bottles used in the adsorption and coprecipitation procedures and all glassware were acid-washed. Mylar film (6.5 μm thick) was employed in the sample holder as sample support for loaded filters (filterpaper Whatman 41, 27 mm diameter).

Apparatus

The instrument used for the measurement of As in charcoal was an ACAX 300 EDXRF spectrometer equipped with a solid state Si(Li) detector and a microcomputer for the data handling and instrument control. The sample was excited with an annular ^{109}Cd 25 mCi (22.1 keV) radioisotope source and its XRF spectrum was measured in 2048 microchannels. The measurement of arsenic in filtrates were carried out with a Varian SpectrAA 400 atomic absorption spectrometer (Victoria, Australia), using either a vapour generation accessory (VGA-76) which employs continuous flow techniques or a GTA 96 graphite tube atomizer for the atomization. A hollow cathode lamp was used for the measurement of As, and background correction was not necessary. The pyrolytic graphite coated tubes were used for GFAAS determinations.

Procedures

Preparation of activated charcoal loaded with metal (MC*). MC* was prepared according to a published method.[7] The modifier metal salt was dissolved in 100 mL water where it formed a colloid precipitate with NaOH solution. 10 g of activated charcoal was put into 100 mL of the modifier metal salt solution and the suspension was stirred with a magnetic stirrer at room temperature for three days. The resulting material (MC*) was filtered off, washed with water and dried at 60 °C overnight.

Sample preparation. If not mentioned otherwise, the samples were prepared as follows: A known volume of standard stock solution was diluted to 100 mL with ultrapure water in a polyethylene leaching bottle. If necessary, the pH of the sample solution was adjusted with NaOH or HNO_3 solution. MC* (0.100 g) was added to the sample and the sample solution was carefully stirred and set aside (15 min) until filtration. The loaded filter was dried at room temperature overnight for XRF determinations, while the filtrate was stored in a polyethylene bottle for vapour generation atomic absorption spectrometry (VGAAS) or GFAAS determination. Four replicates for each sample were prepared if not otherwise mentioned.

Separation procedure. Step 1 (VC* adsorption): The pH of the sample solution was adjusted to 6.0±0.2 with NaOH or HNO_3 solution. VC* (0.100 g) was added to the sample and, after stirring, the mixture was left to stand before filtration. The loaded filter was air dried at room temperature overnight. Step 2 (LaC* adsorption): The filtrate was poured into a second polyethylene leaching bottle and a similar procedure was followed as in step 1 except that the pH of the sample was adjusted to 7.0 ± 0.2 and LaC* (0.100 g) was added. Step 3 (APDC coprecipitation): The filtrate was poured into a third PE leaching bottle. The pH of the sample solution was adjusted to 4.0 ± 0.2 with NaOH or HNO_3 solution. APDC (30 mg) was added to the sample and, after shaking Fe^{3+} carrier (2.8 mg) was added. The precipitate that formed was allowed to coagulate for at least 20 min, after which 0.100 g of activated charcoal powder was added. The mixture was shaken and left to stand before filtration. Step 4 (ZrC* adsorption): The filtrate was poured into a fourth PE leaching bottle. The procedure was similar to that of steps 1 and 2 except that the pH of the sample solution was adjusted to 7.0 ± 0.2 and ZrC* (0.100 g) was added.

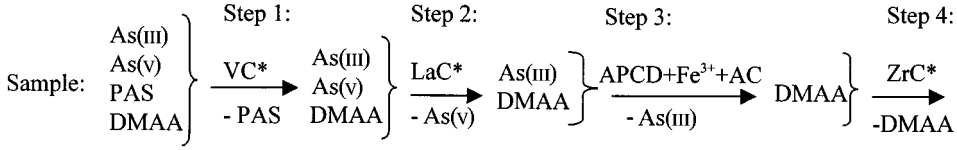
EDXRF. The loaded filters were placed between two Mylar sheets (6.3 μm thick) and moved to a sample holder. The Kα radiation of arsenic (10.53 keV) was measured by EDXRF by using the region of interest (ROI) of 300 eV and the counting time of 100 s. Each sample was measured twice, with the sample being turned about 90° between measurements to avoid the effect of any inhomogeneity of the sample layer on the filter. The mean value of two measurements was taken.

Calibration standards were prepared by diluting a known volume of the standard stock solutions of arsenic (As(v), As(III), DMAA, PAS) to 0.100 mg L with pure water. Arsenic concentrations of 0.5–10.0 mg L^{-1} were used and five replicates were prepared of each. Blanks and calibration standards was prepared as described above.

AAS. The atomic absorption spectrometric (AAS) determinations of arsenic in solution were performed using wavelength 193.7 nm and slit width 0.5 nm. Arsenic standards for calibration of the AAS device were prepared from the arsenic(v) stock solution by diluting this with pure water. All arsenic species are measured by GFAAS. If more than one arsenic species exists in the same sample the value represents the total amount of arsenic in the sample. In the GFAAS determinations, the ashing temperature was 1100 °C, the ashing time 10 s, the atomization temperature 2400 °C and the measurement time 2.0 s. Two replicate measurements were made. 5 μl of 50 ppm Ni solution was used as the matrix modifier. Hydride AAS (HAAS) gives greater accuracy than GFAAS, but organic species cannot be measured. As(v) had to be reduced to As(III) before measurement and the reduction was carried out with potassium iodide at a concentration of 1% w/v with acidic samples (2 mol L^{-1} HCl). The reduction time was 50 min. In the HAAS determinations, $NaBH_4$ was used as the reducing agent and solutions were in 6 M HCl.

Results and discussion

Adsorption by activated carbon is frequently the most efficient and most economical method for removing impurities from water, particularly when the impurities are present in low concentration. Unloaded activated charcoal is not an efficient adsorbent for arsenic, however: As(III) and organic species do not adsorb at all (< 5%), and only about 10–20% As(v) adsorbs if the pH of the sample solution is between 2 and 8.[5] The presence of active metal on the impregnated activated charcoal surface changes the adsorption capability towards both inorganic and organic arsenic species.[6]



Scheme 1 Procedure for the separation of arsenic species

Adsorption of arsenic onto metal-loaded activated charcoal

A study was made of the effect on the adsorption of arsenic species when the activated charcoal surface was loaded with different modifier metals. The activated charcoal was separately loaded with Al, Cr(III), Fe, Hf, Mn, W, Ce, La, Ti, V, In and Zr and a study was made of the adsorption of arsenic species (5 ppm As) in aqueous solution (V = 0.100 L) onto 0.100 g of MC*. The arsenic species were both inorganic [As(III) and As(V)] and organic (DMAA and PAS). The pH of the sample solution was adjusted to 4.0. The Kα radiation of arsenic in the loaded filters was measured by EDXRF. The amount of unadsorbed arsenic was determined by VGAAS or GFAAS. All the modified charcoals adsorbed PAS almost quantitatively, and VC*, MnC*, WC* and CeC* adsorbed only PAS. LaC* adsorbed both PAS and As(V) quantitatively, but did not adsorb As(III) or DMAA at all. AlC* , CrC*, HfC*, InC* and FeC* adsorbed both PAS and As(V) almost quantitatively but As(III) and DMAA only partly (adsorption percentage 10 to 60%). TiC* and ZrC* adsorbed all the arsenic species reasonably well.

On the basis of the preliminary studies LaC*, TiC*, VC* and ZrC* were selected for further study. The effects of the amount of adsorbent and the amount of modifier metal and the pH of the sample solution on the adsorption of arsenic onto MC* were studied to achieve optimal collection and EDXRF measurement conditions. The most suitable amount of MC* for EDXRF determinations was found to be 0.100 g. With a smaller amount the sample was not homogeneously distributed on the filter and with a larger amount the loaded filter was difficult to handle because of the greater thickness of MC* on the filter and the heavier matrix. The effect of the amount of modifier metal M was studied in the range 0.55 to 2.20 mmol M per g C*. The most suitable amount of metal was 2.20 mmol M per g C* for all MC* except ZrC*, for which the most suitable amount was 1.10 mmol Zr per g C*.

The effect of solution pH was studied in the range 1 to 11. The pH was adjusted with HNO_3 or NaOH solution. Fig. 1 shows the percentage of the arsenic species adsorbed as a function of the pH of the sample solution. VC* adsorbed PAS almost quantitatively (>95%) and no other species at any pH. Thus VC* can be used to separate PAS from other arsenic species. LaC* adsorbed PAS and As(V) quantitatively when the pH was between 4 and 10, and not DMAA or As(III) at all. LaC* can thus be used for the separation of PAS and As(V) from As(III) and DMAA. ZrC* adsorbed all arsenic species almost quantitatively (>95%), and the pH of the sample solution had no effect on the adsorption of As(III), As(V) or PAS at pH < 10. The behaviour of DMAA differed from that of the other arsenic compounds: the most suitable pH range for DMAA adsorption onto ZrC* was from 3 to 7, where the recovery was more or less constant and quantitative. TiC* adsorbed As(III), As(V) and PAS almost quantitatively (>95%) when the pH of the sample solution varied from 2 to 9 and only slightly less at lower and higher pH values. The adsorption of DMAA onto TiC* was a little poorer (>85%)

Coprecipitation of As(III) with APDC

As(III) and DMAA behaved so similarly on all the MC* investigated that they could not be separated from each other by use of MC* alone. Accordingly, a study was made of the separation of As(III) from DMAA by coprecipitation of As(III) with APDC, with Fe^{3+} acting as carrier[8,9], and subsequent adsorption onto activated charcoal (0.100 g). The effects of the amount of iron carrier (1.4–4.4 mg) and APDC (10–150 mg) were studied separately, with one or the other component kept constant (Fe^{3+} 2.8 mg and APDC 30.0 mg). The pH of the As(III) samples (1 ppm As, V = 0.100 L) was adjusted to 4.0. The amounts of the iron carrier and APDC had no great effect on the adsorption of As(III) so 2.8 mg Fe^{3+} and 30.0 mg APDC were chosen for further investigation. Study of the effect of the pH of the sample solution on the APDC coprecipitation showed that the pH affects the adsorption of As(III) dramatically (Fig. 2). The adsorption of As(III) remained at constant level when the pH of the sample solution was lower than 4.0. DMAA was not adsorbed at any pH with APCD coprecipitation.

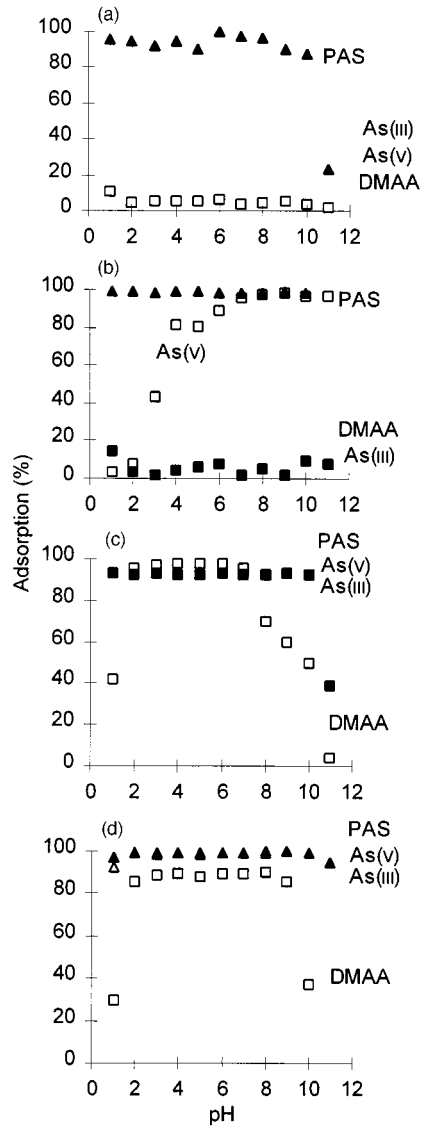


Fig. 1 Recoveries of As as a function of pH of the sample solution, when the collector was (a) VC*, (b) LaC*, (c) ZrC*, (d) TiC* (1.0 mg As L^{-1}, V = 0.1 L, m(MC*) = 0.100 g, n = 4, GFAAS).

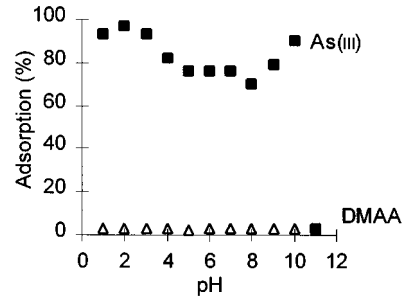


Fig. 2 Recoveries of As as a function of pH of the sample solution when APDC coprecipitation was used (1.0 mg As L^{-1}, V = 0.1 L, m(APDC) = 30 mg, m(Fe^{3+}) = 2.8 mg, m(AC) = 0.100 g, n = 4, GFAAS).

Separation and determination of arsenic species

LaC*, ZrC* and VC* can be used for the separation of the investigated arsenic species from each other. In the case of VC* only PAS was quantitatively adsorbed onto MC*. With LaC* used as collector, As(v) was almost quantitatively separated from As(iii) and DMAA. As(iii) can be separated from DMAA by using ammonium salt of APCD in the presence of an excess of a carrier ion,[5] and DMAA can be collected onto ZrC*.

Calibration graphs (0.5–10.0 mg As L^{-1}) for EDXRF determinations were prepared separately for each collection step by using a particular arsenic species and a particular MC* as described above. Five replicates were prepared for each standard. The Kα radiation intensity of arsenic in loaded filters was measured by EDXRF, and the regression line was calculated from the experimental data for the linear part of each calibration graph. Values of m (sensitivity), b (background) and the correlation coefficient for the regression lines ($y = mx + b$) of each arsenic species are given in Table 1. In the equation, y is the net count rate (counts s^{-1}) and x is the amount of arsenic in mg L^{-1}. Table 1 also presents the detection limits calculated as DL = $(3/m)(b/t)$,[1/2] where t is the measurement time (100 s), and the maximum value of the linear range.

The procedure developed for the separation and determination of the different arsenic species was tested on five synthetic samples containing 1.0 mg L^{-1} of each arsenic species for a total arsenic concentration of 4.0 mg L^{-1}. Samples were carried through the separation procedure described above and the Kα radiation intensity of the collected arsenic species in MC* was measured. The recoveries of the arsenic species were calculated and are shown in Table 2 with 95% confidence limits and the RSD. The recovery of the different arsenic species was quantitative, indicating that they were separated and collected quantitatively. The precision of the procedure is good estimated from the RSD value. The RSD value of five replicate samples was below 3% for all arsenic species at a 1.0 mg L^{-1} concentration level. The results show that the procedure is well suited for the separation, concentration and determination of As(iii), As(v), PAS and DMAA in sample solutions.

Table 1 Analytical parameters of EDXRF measurements of arsenic species on metal collectors (V = 0.1 L, t = 100 s, n = 4)

	PAS	As(v)	As(iii)	DMAA
Collector	VC*	LaC*	APDC	ZrC*
Sensitivity (m)/counts (s mg L)$^{-1}$	26.23	26.03	21.76	26.42
Background (b)/counts s^{-1}	0.45	0.77	1.92	0.71
Correlation coefficient (r)	0.9995	0.9991	0.9971	0.9993
Detection limit (DL)/mg L^{-1}	0.008	0.010	0.019	0.010
Linear range/mg L^{-1}	6.0	10.0	3.5	3.0

Table 2 Recovery of arsenic (1 mg L^{-1} each of As(v), As(iii), PAS and DMAA, n = 5, EDXRF) by adsorption on a metal collector

Order of separation steps	Species	Recovery (%)	RSD%
1. VC* adsorption	PAS	103 ± 6	2.1
2. LaC* adsorption	As(v)	100 ± 3	1.2
3. APDC coprec.	As(iii)	106 ± 6	2.8
4. ZrC* adsorption	DMAA	101 ± 8	1.6

Conclusions

The presence of metal on the surface of activated charcoal affects the adsorption capability of the charcoal significantly. VC*, MnC*, WC* and CeC* adsorbed PAS quantitatively, and none of the other arsenic species at all. LaC* adsorbed efficiently both PAS and As(v) but not As(iii) or DMAA. TiC* and ZrC* adsorbed all arsenic species quantitatively and made suitable collectors for total arsenic.

The four-step procedure that was developed is well suited for the separation, concentration and determination of As(v), As(iii), PAS and DMAA in the same sample solution. Previous approaches proposed for the specification and determination of arsenic species are complex combinations of methods. Typically, the separation of arsenic species in aqueous solutions is accomplished by HPLC and concentrations are determined by ICP-AES, ICP-MS or GFAAS. These techniques are expensive, and time consuming and well-trained personnel are required. Our method is simple and relatively rapid, inexpensive and of good precision and accuracy. The same sample can be measured several times and stored for further measurements and, if necessary, the arsenic species can be removed from the MC* and subsequently reanalysed by another method. Although the arsenic concentrations in environmental waters will usually be too low to allow EDXRF determination, the method is suitable for industrial wastewaters.

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