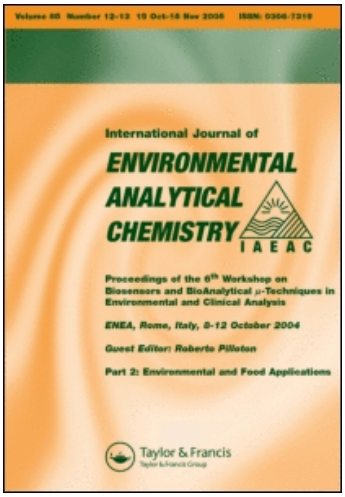

International Journal of Environmental Analytical Chemistry
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713640455

Solid-Phase Extraction of As(III) from Aqueous Samples Using On-Column Formation of As(III)-Trispyrrolidinedithiocarbamate

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To cite this Article Van Elteren, J. T. , Gruter, G. J. M. , Das, H. A. and Brinkman, U. A. Th.(1991) 'Solid-Phase Extraction of As(III) from Aqueous Samples Using On-Column Formation of As(III)-Trispyrrolidinedithiocarbamate', International Journal of Environmental Analytical Chemistry, 43: 1, 41 — 54
To link to this Article: DOI: 10.1080/03067319108028118
URL: http://dx.doi.org/10.1080/03067319108028118

Intern. J. Environ. Anal. Chem., Vol. 43, pp. 41–54
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SOLID-PHASE EXTRACTION OF As(III) FROM AQUEOUS SAMPLES USING ON-COLUMN FORMATION OF As(III)-TRISPYRROLIDINEDITHIOCARBAMATE

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(*Received 29 June 1990*)

Two methods are presented for the selective preconcentration of As(III) by using complexation-type stationary phases. These phases are prepared: (1) by loading a C18-bonded silica with the cetyltrimethylammonium–pyrrolidinedithiocarbamate (CTA^+–PDC^-) ion-pair, or (2) by converting a strong anion-exchange (SAX) resin from the quaternary ammonium form into the pyrrolidinedithiocarbamate (PDC^-) form. When As(III)-containing solutions are passed through such stationary phases, the immobilized PDC^- yields the non-polar As(III)-trispyrrolidinedithiocarbamate ($As(PDC)_3$) which is retained on the non-loaded second part of the C18 cartridge (method 1), or on an unloaded C18 cartridge coupled in series with the SAX cartridge (method 2).

For both methods parameters influencing the preconcentration have been investigated by using the $^{74}As(III)$ radiotracer; $^{74}As(V)$ was applied to study the selectivity of both methods. A selective preconcentration of As(III) is possible. The retention mechanisms are discussed. After optimization, the applicability was tested by determining As(III) in some real water samples. To this end the $As(PDC)_3$ was eluted from the C18 cartridges with acetone, followed by evaporation and redissolution in a suitable solvent for hydride generation atomic absorption spectrometry (HGAAS). Arsenic can be determined in both fresh water and seawater satisfactorily with a detection limit of about 0.02 ng ml^{-1}.

INTRODUCTION

Today, much attention is focused on the speciation of arsenic in environmental waters, as toxicity varies widely with valency and molecular form.[1] Therefore, determination of the total concentration of arsenic is no longer satisfactory, but differentiation between arsenic species is necessary. Most attention is paid to As(III), as this is the most toxic arsenic species. Generally, solvent extraction techniques are used to selectively extract As(III) from solution;[2–7] in the presence of a chelating agent, As(III) is complexated and extracted into an organic solvent. EDTA is often added to the sample solution to mask interferences from heavy metal ions. Either direct analysis of the organic extract (by graphite furnace atomic

absorption spectrometry [GFAAS]) or indirect analysis after mineralization (by hydride generation atomic absorption spectrometry [HGAAS]) or after back-extraction (by GFAAS or neutron activation analysis [NAA]) has been performed.

In the past decade a shift from rather laborious solvent extraction procedures to faster column techniques has taken place. Leyden *et al.*[8–10] synthesized suitable stationary phases by immobilizing complexing agents on silica. Later such phases were applied in columns for the preconcentration of As(III) by using mercapto-modified silica, followed by detection of As(III) with HGAAS[11] and by using thionalide-loaded silica, followed by determination with silver diethyldithiocarbamate spectrophotometry.[12]

After the development of silica-bonded phases for solid-phase extraction (SPE),[13] metal complexes formed off-line have been preconcentrated on several non-polar cartridges prior to NAA[14] or HPLC separation with UV/VIS detection.[15,16] However, off-line formation of these non-polar metal complexes results in losses due to adsorption of these compounds on the walls of vessels, tubing, etc.[15,17,18] This problem has been overcome by on-column formation of the metal complexes after loading the complexing agent on the column as a first step,[17] followed by preconcentration of the metals, with subsequent elution and on-line separation.[18]

In this work two methods are described for the selective preconcentration of As(III) in aqueous samples by using complexation with dithiocarbamates.[19] Preconcentration of As(III) is accomplished by using (1) C18-bonded silica loaded with the cetyltrimethylammonium–pyrrolidinedithiocarbamate (CTA^+–PDC^-) ion-pair or (2) a strong anion-exchange (SAX) resin converted into the PDC^- form and coupled in series with an unloaded C18 cartridge. In Table 1 additional information about the reagents used for loading of the commercially available SPE cartridges is given. Optimization of both methods and investigation of the retention mechanism was carried out by using the ^{74}As(III)-radiotracer. ^{74}As(V) was applied to study the selectivity of the preconcentration methods. For the determination of As(III) in some real water samples the eluates were subjected to HGAAS.

EXPERIMENTAL

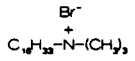
Materials

The solid-phase extraction materials used were Sep-Pak C18 cartridges (weight of packing: ca. 0.4 g) from Waters Associates and SAX cartridges containing 100 mg of a strong (quaternary ammonium) anion exchanger from J. T. Baker.

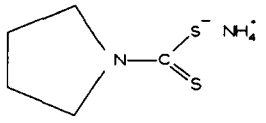
Deionized water was obtained by processing demineralized water in an ion-exchange unit connected to a 0.2 μm filter assembly (Barnstead ultra pure water system). All glassware was rinsed with dilute nitric acid and repeatedly washed with deionized water before use. Preliminary experiments showed that no problems were to be expected by using glassware in the arsenic determination.

Ammonium pyrrolidinedithiocarbamate (APDC) p.a. from Merck and cetyltri-

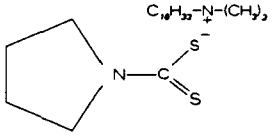
Table 1 Reagents used for loading of the cartridges



Cetyltrimethylammonium bromide (CTAB)



Ammonium pyrrolidinedithiocarbamate (APDC)



Cetyltrimethylammonium–pyrrolidinedithiocarbamate (CTA^+–PDC^-)

methylammonium bromide from Samenwerkende Farmaceutische Groothandelaren were dissolved in deionized water to form the CTA^+–PDC^- ion-pair. Disodium ethylenediaminetetraacetic acid p.a. (EDTA) from J. T. Baker was used in masking studies; a stock solution of 6% (w/w) in deionized water was prepared. Arsenic stock solutions (1000 $\mu g\,ml^{-1}$ in 1 M HCl were made by dissolution of As_2O_3 (Aldrich) and dilution of an As_2O_5 Titrisol standard solution (Merck), respectively. Dilution of the arsenic stock solutions with 1 M HCl yielded the proper working solutions.

^{74}As ($t_{1/2} = 17.8$ days, $E = 596$ keV) was purchased from Amersham in the pentavalent state; ^{74}As(III) was prepared by reduction of ^{74}As(V) with a mixture of KI/ascorbic acid under strongly acidic conditions,[20] after which the pH was raised to 4 for reasons of stability.

All other reagents were of analytical reagent grade. For studying anionic and cationic interferences, samples containing the individual interfering ions were prepared at concentration levels higher than to be expected in environmental waters.

Apparatus

A system as outlined in Figure 1 was used to study the breakthrough of pyrrolidinedithiocarbamate during loading of (1) a C18 cartridge with the CTA^+–PDC^- ion-pair or (2) a SAX cartridge with PDC^-. With a four-way valve (Whitey) the appropriate solutions (methanol/deionized water for conditioning, loading solution [CTA^+–PDC^- ion-pair or PDC^-] and HNO_3 solutions for

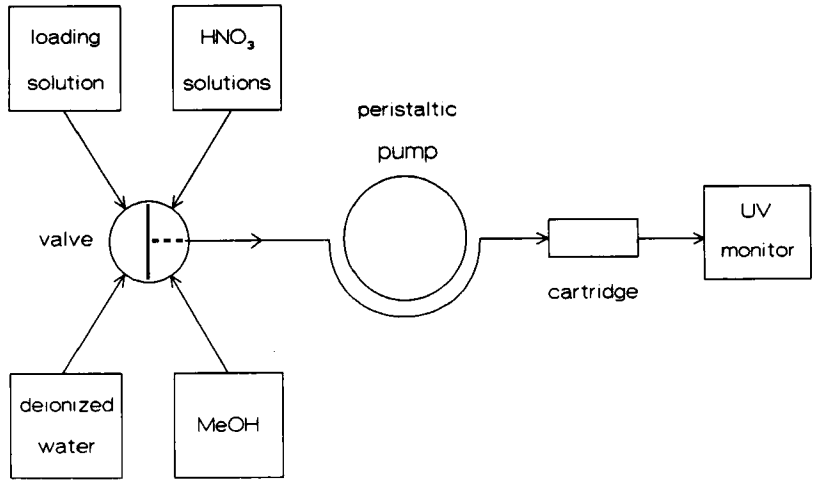


Figure 1 System configuration for experiments on cartridge loading.

stability studies) were selected and pumped peristaltically (Gilson minipuls 2) through the cartridges to a Hitachi 755A-22 Variable Wavelength UV monitor. The absorbance of pyrrolidinedithiocarbamate at 254 nm was recorded on a strip-chart recorder (Kipp & Zonen BD 8 multi range recorder); CTA^+ does not absorb at this wavelength. For reasons of convenience, in subsequent studies a Baker SPE-21 system was used to pass the solutions through the cartridges.

Testing of both methods was carried out using radiotracers. After preconcentration the cartridges containing the activity were counted on a NaI detector (Philips PW 4580 Automatic Gamma Analyzer) in the range 200–2000 keV. Recoveries were calculated by comparison with references. The counting time was selected in such a way, that relative standard deviations due to counting statistics were smaller than 1%.

To test the applicability of both methods for the selective preconcentration of As(III) in water samples, detection of the cartridge eluates was done by means of HGAAS (for details, see below).

Procedure for Real Water Samples

Sample preparation

Sea-water from the North Sea, and fresh surface water from the Noordhollands Kanaal, were collected in 25 l polyethylene containers; after filtration (0.45 μm) the water was acidified to pH ca. 2 with HNO_3.

Selective As(III) preconcentration

Both the C18 cartridge in method 1 and the SAX-C18 cartridge combination in

method 2 were conditioned with 5 ml of methanol and 5 ml of deionized water. Subsequently the C18 cartridge was loaded with the ion-pair CTA^+–PDC^- formed off-line and the SAX-C18 cartridge combination with PDC^-. After flushing the C18 cartridge and the SAX-C18 cartridge combination with 5 ml of 0.01 M HNO_3 solution, the sample solution was passed through the cartridges. Rinsing was done with 10 ml of 0.01 M HNO_3.

When standard solutions containing $^{74}As(III)$ were passed through the loaded cartridges at different flow rates, the As(III) recovery was found to be independent of flow rate up to 25 ml min^{-1} for method 1. For method 2 the back pressure of the cartridge combination made it impossible to reach flow rates higher than 10 ml min^{-1}. Under optimized conditions the recovery of As(III) was over 99% in all cases when standard solutions were considered.

HGAAS detection

For both methods, the C18 cartridges containing the preconcentrated As(III) were eluted in reverse direction with 5 ml of acetone; the SAX cartridges used in method 2 were discarded. It is advisable to elute the cartridges immediately after preconcentration as storage (even for 1 day) leads to incomplete elution. The eluates were collected in 10 ml glass volumetric flasks. After evaporation of the acetone to dryness with an He stream, the volume was made up to the mark with 2 M HCl. Radiotracer experiments showed that no losses occur due to elution and evaporation.

Arsenic present in the eluates was determined by HGAAS. A home-made hydride generation system connected to a modified atomic absorption spectrometer, optimized for the measurement of arsenic, was used for the analyses.[21] In the continuous flow mode 8.3 ml min^{-1} sample and 4.7 ml min^{-1} 0.7% [w/v] $NaBH_4$ (stabilized by 0.4% [w/v] NaOH) are mixed, resulting in generation or arsine (AsH_3). In a gas-liquid separator the arsine is separated from the liquid and transported (with 80 ml min^{-1} of N_2 and 18 ml min^{-1} of air) to an electrically heated quartz cuvette (ca. 800 °C), aligned in the lightpath (EDL) of the atomic absorption spectrometer. Air is added because oxygen enhances the atomization or arsine.[22]

Handling of eluates is the same as for routine measurements.[21] This means that a standard reduction step with KI/ascorbic acid under strongly acidic conditions is performed to be sure that all arsenic is in the trivalent state, because As(V) resulting from oxidation during storge cannot be completely converted into arsine in the hydride generation system used. To this end usually 4-ml aliquots from the flasks are taken and the following reagents added: 1.5 ml of 9 M H_2SO_4, 0.75 ml of 20% [w/v] KI and 0.3 ml of 20% [w/v] L(+)-ascorbic acid. Other 4-ml aliquots from the same flasks were spiked with 10 ng of As_2O_5 (0.5 ml of 20 ng ml^{-1} As_2O_5 solution) and taken through the same standard reduction step. Absorbance signals from both sample and spiked sample are used to calculate the amount of arsenic in the sample.

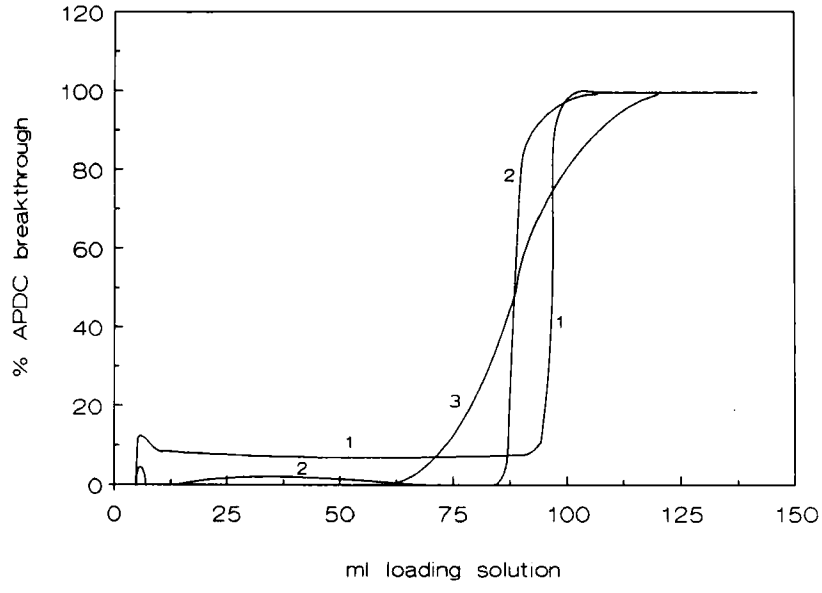


Figure 2 Breakthrough of PDC^- for a ca. 0.4 g C18 cartridge as a function of the amount of ion-pair loading (in ml). Loading solution composition: (1) 2.0×10^{-3} M $CTA^+ + 2.0 \times 10^{-3}$ M PDC^-; (2) 2.8×10^{-3} M $CTA^+ + 2.0 \times 10^{-3}$ M PDC^-; (3) 4.0×10^{-3} M $CTA^+ + 2.0 \times 10^{-3}$ M PDC^-.

RESULTS AND DISCUSSION

Breakthrough Capacity During Cartridge Loading

For method 1, the loading of the CTA^+–PDC^- ion-pair on a C18 cartridge and the breakthrough were studied by using the experimental design shown in Figure 1. Different mixing ratios of CTA^+ and PDC^- were used to find an ion-pair composition for loading pyrrolidinedithiocarbamate on the cartridges efficiently. The following millimolar CTA^+:PDC^- ratios were mixed off-line in 1 litre of deionized water: 2:2, 2.8:2 and 4:2. A millimolar concentration level was chosen because CTA^+ is not soluble at higher concentrations; in the literature, the use of a free CTA^+ concentration below the critical micellar concentration of 0.9 mM is recommended.[23] During loading, the effluent from the cartridge was continuously monitored at 254 nm until 100% breakthrough of pyrrolidinedithiocarbamate occurred. The CTA^+–PDC^- ion-pair formed off-line is efficiently adsorbed on the C18 surface, as is evident from the breakthrough curves presented in Figure 2. A solution containing 2.8 mM CTA^+ and 2 mM PDC^- results in the most efficient loading. Higher CTA^+ concentrations cause faster breakthrough due to competitive CTA^+ adsorption on the C18 surface. Lower CTA^+ concentrations give rise to incomplete ion-pair formation and, therefore, breakthrough of pyrrolidinedithiocarbamate. Calculations show that the maximum loading capacity of the ca. 0.4 g C18 cartridges for the CTA^+–PDC^- ion-pair is about 100 mg.

Finally, cartridges completely loaded with the ion-pair were flushed with solutions of different HNO_3 molarity to evaluate the stability of the CTA^+–PDC^- on the cartridges. It was observed that the amount of CTA^+–PDC^- ion-pair remaining on the cartridge decreases with increasing acidity (however, in actual practice no capacity problems occur down to pH = 1). An explanation for this phenomenon is instability of the ion-pair as a result of protonation and/or decomposition of PDC^-. Protonation will lead to the formation of HPDC which is, to some extent, also retained on the C18 surface; this means that a slight chelating capacity will remain. Decomposition will give rise to the formation of C_4H_9N and CS_2, so that the chelating capacity is completely lost.

For method 2, a solution of 2 mM PDC^- in deionized water was used for the loading of the SAX cartridges. From the breakthrough curve the maximum loading capacity of the 100 mg SAX cartridges for PDC^- was calculated to be about 50 mg. Flushing with acidic solutions resulted in loss of pyrrolidinedithiocarbamate from the cartridges due to the same causes as discussed for method 1.

In the following experiments 50 ml 0.01 M HNO_3 solutions, containing 20 ng ml^{-1} of As(III) and a ^{74}As(III) spike, were used as standard samples unless stated otherwise.

Recovery of ^{74}As(III) as a Function of the Degree of Loading

Various volumes of CTA^+–PDC^- loading solution were used for loading the C18 cartridges according to method 1, after which standard samples were preconcentrated on these cartridges. The results are given in Figure 3. In order to obtain high As(III) recoveries, the CTA^+–PDC^- loading of the cartridge obviously should not be over 40%. The explanation for this phenomenon is that, if the C18 surface becomes too highly loaded with the CTA^+–PDC^- ion-pair, less free C18 surface is available for $As(PDC)_3$ retention. This was confirmed by the following experiment. A C18 cartridge was loaded for 25% with CTA^+–PDC^- and the sample solution was passed through this cartridge from the opposite direction. In contrast with the result of the normal preconcentration procedure, the recovery in this case was only 6% because hardly any free C18 surface is available after complexation of As(III) to $As(PDC)_3$.

In the next experiments the C18 cartridges used in method 1 were partially loaded, i.e., with 25 ml of a loading solution containing 2.8 mM CTA^+ and 2 mM PDC^-. This corresponds to 25% loading relative to maximum loading.

For method 2—with its two separate cartridges—the above considerations are irrelevant. As can be expected, the retention of ^{74}As(III) on the unloaded C18 cartridge coupled in series with a SAX cartridge does not decrease with high PDC^- loading. The amount of ^{74}As(III) retained on the SAX cartridge is negligible (< 1%). In all further experiments 5 ml of a 2 mM PDC^- solution was used to load the SAX-C18 cartridge combination.

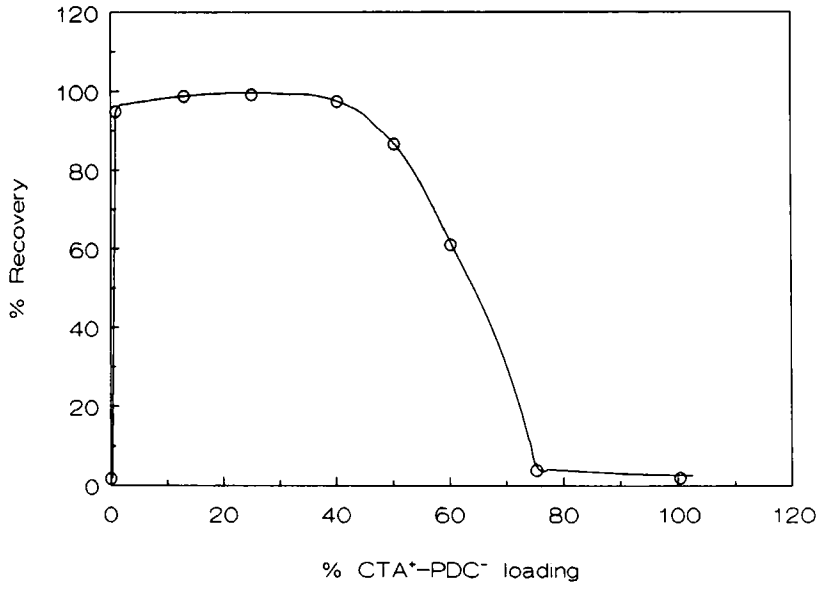


Figure 3 Recovery of As(III) as a function of the relative amount of CTA^+–PDC^- loading with a loading solution containing 2.8 mM CTA^+ and 2 mM PDC^-.

Recovery of $^{74}As(III)$ as a Function of the pH

The influence of the acidity of the sample solution on the $^{74}As(III)$ recovery was studied by means of method 1. To this end standard samples were adjusted with HNO_3 and NaOH to various pH values varying between 1.5 and 12 (no oxidation of As(III) occurs at these pH values during preconcentration). Results are shown in Figure 4. At pH values above 5 a sharp decrease in the recovery is observed as a result of inefficient $As(PDC)_3$ formation at higher pH values.

Recovery of $^{74}As(III)$ as a Function of Sample Volume and Type

Several acidified real water samples were spiked with $^{74}As(III)$ tracer to study the recovery of As(III) as a function of water type and sample volume. The volume was varied to find the limits for quantitative recovery of As(III). Results for methods 1 and 2 are shown in Table 2. During preconcentrations a gradual coloration of the C18 cartridges was observed which progressed from top to bottom. This is caused by the presence of other heavy metal ions in the water samples used which also form complexes with PDC^- and compete with $As(PDC)_3$ for retention on the C18 surface. The limited capacity of the C18 cartridges causes breakthrough of As(III) when the C18 cartridges are completely coloured and no free surface is available for $As(PDC)_3$ retention any more. With method 1, sample volumes of at least 100 ml can be used for both waters. With method 2, at least 100 ml of Noordhollands Kanaal water and 150 ml of North Sea water can be used. To have a safe margin for breakthrough of As(III) in a real water sample, volumes of 50 ml were used in further experiments.

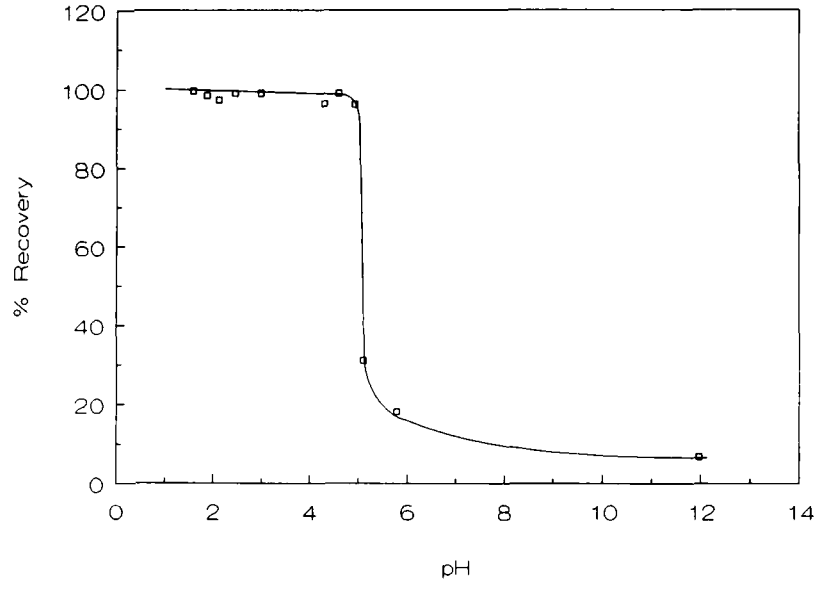


Figure 4 Recovery of As(III) as a function of the pH of the sample solution.

Table 2 Recovery of As(III) from spiked surface water samples

Method	*Sample volume (ml)*	*Recovery (%)*	
		Nh. Kanaal water	*North Sea water*
Method 1	25	99	98
	50	99	98
	75	99	98
	100	97	97
	150	72	78
	200	46	50
Method 2[a]	25	96 (1)	97 (0)
	50	95 (1)	97 (0)
	75	95 (0)	98 (1)
	100	96 (1)	96 (1)
	150	83 (1)	96 (2)
	200	10 (0)	29 (1)

[a]The amount of arsenic remaining on the SAX cartridge is given in parentheses.

Table 3 Dependence of As(III) recovery in the presence of foreign ions

Foreign ions	*As(III) recovery (%)*	
	No EDTA	*0.5% (w/w) EDTA*
Metal ions ($10\,\mu g\,ml^{-1}$)		
Cu^{2+}	22	15
Co^{2+}	82	96
Ni^{2+}	96	—
Fe^{3+}	22	21
Cd^{2+}	48	95
Mn^{2+}	97	—
Cr^{3+}	97	—
Hg^{2+}	96	—
Zn^{2+}	98	—
Anions (sodium salts)		
0.1 M Cl^-	100	—
1.0 M Cl^-	99	—
0.1 M HSO_4^-	100	—
0.1 M NO_3^-	92	—

—, Not determined.

Influence of Anions and Cations on the $^{74}As(III)$ Recovery

The dependence of the recovery of $^{74}As(III)$ on the presence of several anions and cations was also studied. Possible suppression of cationic interferences was attempted by adding 0.5% (w/w) EDTA to the samples.[24] Preconcentration was carried out according to method 1 only because for method 2, in the presence of EDTA, the recoveries decreased dramatically, probably due to competition of EDTA with PDC^- for sorption on the SAX surface. The results are given in Table 3. It can be concluded that interferences decrease in the order $Cu^{2+} \simeq Fe^{3+} > Cd^{2+} > Co^{2+}$; the other ions do not seriously interfere at all. Although EDTA improves the recovery of As(III) in the case of Cd^{2+} and Co^{2+}, the interferences caused by Cu^{2+} and Fe^{3+} are not suppressed. However, the concentration levels studied are much higher than can be expected in real samples where $^{74}As(III)$ recoveries are quantitative as can be seen from Table 2. For this reason EDTA addition to real water samples is not recommended.

Inorganic Arsenic Speciation

In order to study the selectivity of both methods for inorganic arsenic speciation, 50 ml of solutions containing As(III) or As(V), were preconcentrated. The concentration of each species was $20\,ng\,ml^{-1}$. ^{74}As tracer was added in the same valency state as the inactive species. The results are shown in Table 4. It can be concluded that the methods quantitatively discriminate between As(III) and As(V).

Table 4 Recovery of As(III) and As(V)

Arsenic species	*Recovery* (%)	
	Method 1	*Method 2*[a]
As(III)	99.7	97.4 (<1)
	97.9	98.7 (<1)
As(V)	<1	<1 (<1)
	<1	<1 (<1)

[a]The amount of arsenic remaining on the SAX cartridge is given in parentheses.

Proposed Retention Mechanisms

The retention mechanisms proposed for methods 1 and 2 are schematically shown in Figure 5.

Method 1 The ion-pair CTA^+–PDC^- is formed off-line in deionized water, followed by its sorption on the C18 surface. In the acidified sample solution, the following equilibrium exists:

$$AsO_3^{3-} + 6H^+ \rightleftarrows 3H_2O + As^{3+}. \quad (1)$$

This equilibrium completely shifts to the right-hand side by complex formation of As^{3+} with PDC^-:

$$As^{3+} + CTA^+\text{–}PDC^- \rightarrow As(PDC)^{2+} + CTA^+ \quad (2a)$$

$$As(PDC)^{2+} + CTA^+\text{–}PDC^- \rightarrow As(PDC)_2^+ + CTA^+ \quad (2b)$$

$$As(PDC)_2^+ + CTA^+\text{–}PDC^- \rightarrow As(PDC)_3 + CTA^+. \quad (2c)$$

The As-containing species resulting from reactions (2a) and (2b) are ionic and are therefore not retained on the C18 surface. The non-polar $As(PDC)_3$ species, however, is strongly retained on the C18 surface.

Method 2 A SAX cartridge is loaded with a PDC^- solution; this results in electrostatic bonding of PDC^- to the quaternary ammonium cation. Complex formation takes place in a similar way as described for method 1. The non-polar $As(PDC)_3$ is not retained on the SAX surface, but is trapped on a C18 cartridge coupled on-line with the SAX cartridge.

Results for Real Samples

The applicability of both methods for the determination of arsenic in real water samples was tested using Noordhollands Kanaal water and North Sea water with standard addition of As(III) and HGAAS detection. Preliminary experiments showed that, with method 1, special precautions have to be taken, as the presence

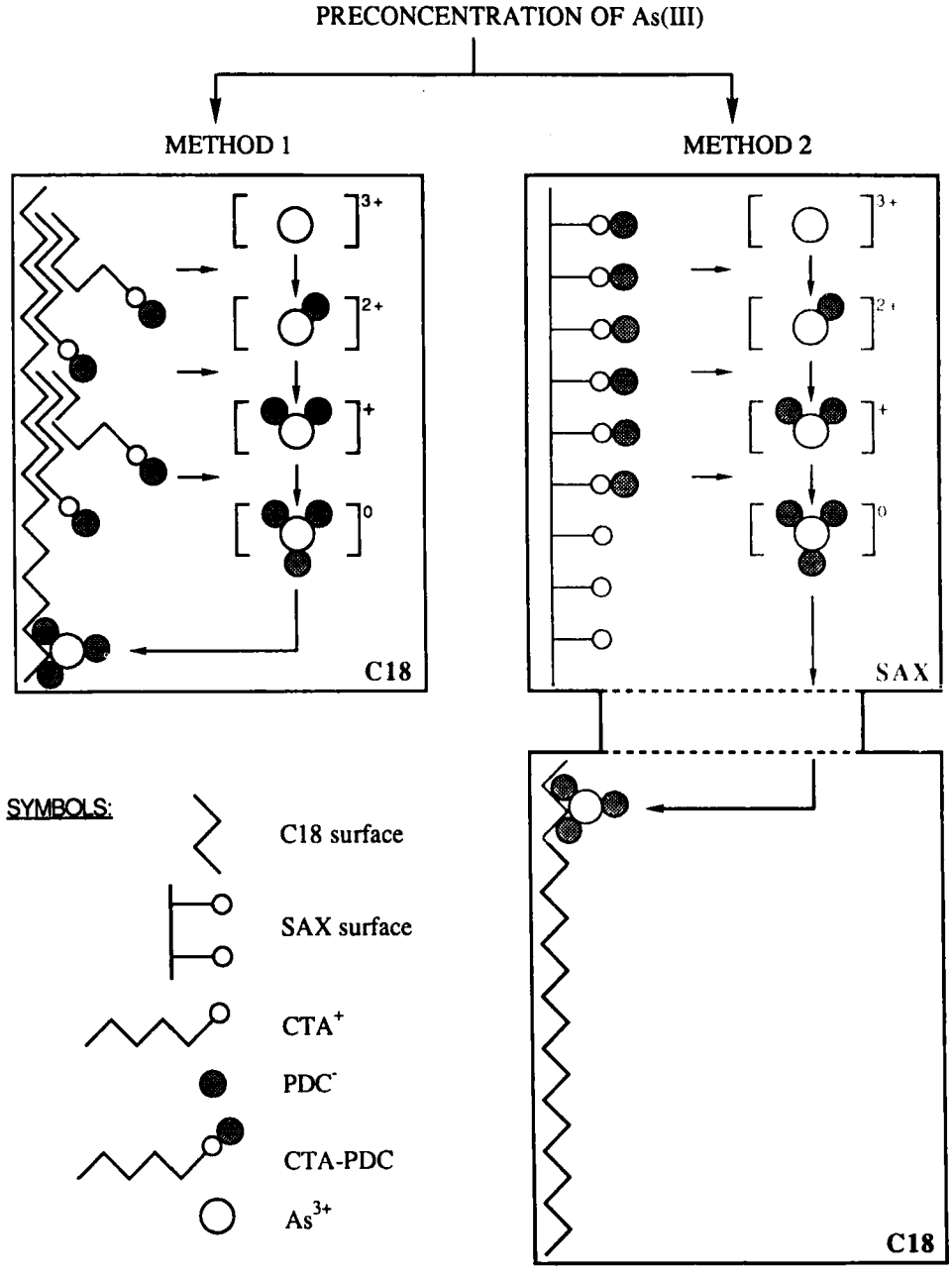


Figure 5 Proposed retention mechanisms for methods 1 and 2.

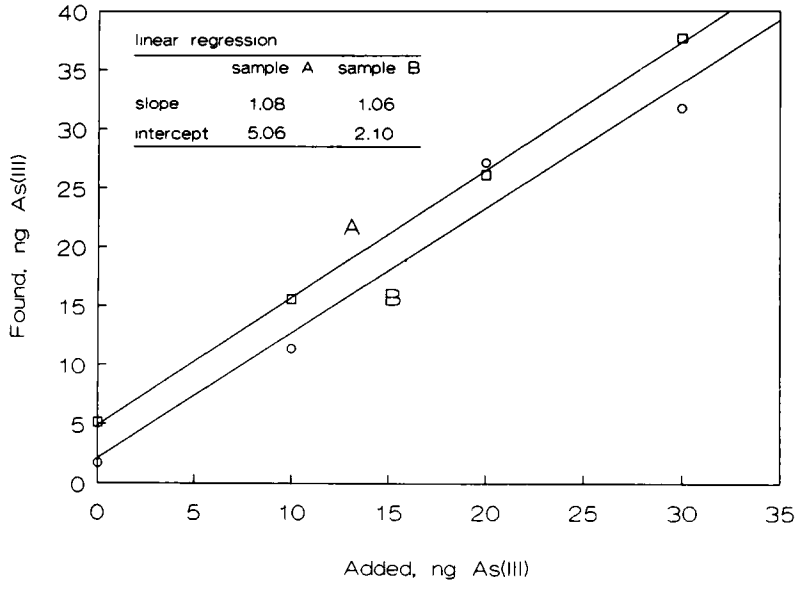


Figure 6 As(III) determination in 50 ml of (A) Noordhollands Kanaal water and (B) North Sea water using standard addition; for experimental details, see text.

of CTA^+ results in foam formation. Therefore, a foam collector was installed just before the quartz cuvette to prevent deterioration of the inner surface. However, results remained irreproducible and therefore only method 2 was further investigated. Figure 6 shows the standard addition curves for two samples. From linear regression analysis the slopes and intercepts were calculated to be as given in the figure. Obviously, preconcentration is essentially quantitative in both cases. The As(III) concentrations in Noordhollands Kanaal water and North Sea water are 0.10 and 0.04 ng ml^{-1}, respectively. The detection limit is about 0.02 ng ml^{-1}. Method 2 is simple and fast: cartridge preparation (conditioning and ion-pair loading), sample loading and elution can be carried out on-site in less than 15 minutes using syringes, while evaporation and redissolution can take place in the laboratory. The advantage of this technique—as a result of the on-site complexation—is that speciation alteration upon storage[25] can be prevented. Further studies concerning speciation of methylated arsenic species are in progress.

Acknowledgements

The authors thank Drs. H. Irth and J. B. H. A. van Oppenraaij for valuable suggestions and G. Heeringa for his assistance in the HGAAS measurements.

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