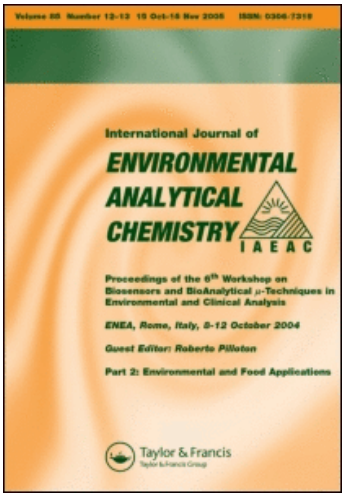

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ON-LINE CHLORIDE INTERFERENCE REMOVAL FOR ARSENIC DETERMINATION IN WASTE WATER AND URINE BY ICP-MS USING A MODIFIED CAPILLARY

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The determination of arsenic in environmental samples like waste waters from industrial effluents and in biological samples like urine is very important due to the toxic nature of some of its species at moderate levels of exposure. The objective of this study was to evaluate the capability of modified anionic capillaries to remove chloride for ICP-MS determination of arsenic, which causes spectral interference due to formation of $^{40}Ar^{35}Cl^{+}$. Also high chloride content gives non-spectral interferences. The results indicate that arsenic at a concentration higher than $1\,\mu g\,L^{-1}$ in a matrix with a chloride content up to $600\,mg\,L^{-1}$ can be accurately determined using a 3-aminopropyltrimethoxysilane (APTMS) modified capillary connected to a micro-concentric nebuliser (MCN). The interference level of chloride is considerably reduced due to its retention in the capillary. The method has been successfully applied and validated for waste water and by recovery tests for urine (diluted 1 : 15) samples.

Keywords: Arsenic; Chloride; ICP-MS; Interferences; Urine; Waste water; Capillaries

INTRODUCTION

ICP-MS is considered to be a powerful and reliable technique for trace determination in body fluids and environmental samples. The major drawback of ICP-MS is that it suffers from several types of spectral and non-spectral interferences [1–4] which limit its application.

Generally, the most effective way to overcome the interferences problem is to separate the disturbing components from the analytes completely before entering the plasma and the mass spectrometer. Chemical pre-treatment, e.g., solvent extraction after complexation [5,6] or ion-exchange [7,8]; has proved to remove several interferences

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successfully, but either technical effort or time consuming [9] off-line analysis limit the applicability of such methods. Other approaches to reduce these interferences are the use of a collision cell or a HR-ICP-MS, but these facilities are not used on a routine basis in the laboratory.

Matrix effects [10–13] are more dominant at low concentration levels and many workers have proposed the use of internal standards for the correction of matrix induced signal variation but the selection of the proper internal standard is not always an easy task and can lead to systematic errors.

The analysis of arsenic in biological and industrial effluents is complicated due to the low concentration of this analyte (about 5–50 $\mu g\,L^{-1}$) and the formation of the argon chloride ($^{40}Ar^{35}Cl^{+}$) molecular ion, which overlaps with monoisotopic arsenic at m/z 75. Among the various approaches given in the literature to overcome this interference are: (1) Mathematical correction by considering the formation of the other molecular ion ($^{40}Ar^{37}Cl^{+}$) under the same experimental conditions. [14–16] (2) Addition of inert gases to the plasma [11,17–20] (3) addition of organic solvents to the standards and samples [11,21–24] (4) using ion exchange resins for the removal of the interfering elements [25]. (5) Coupling of other chromatographic techniques to the ICP-MS [26]. Most of these approaches are quite difficult and not always easy to use.

In previous studies we have developed a new concept for interference removal in ICP-MS analysis by on-line separation of the interfering elements during the sample introduction [27–29]. The surface of commercially available silica capillaries used for sample transport in combination with a microconcentric nebuliser (MCN) was modified chemically in order to retain the chloride interfering ions on the surface. After the measurement, the interfering ions can be easily eluted with a suitable solvent.

In this work the possibilities of this new methodology have been studied for the determination of arsenic in high chloride content samples like human urine and industrial effluents.

EXPERIMENTAL

Instrumentation

An ICP-MS HP 4500 PLUS (Hewlett-Packard, Madrid, Spain) equipped with a Babington nebulizer was used to evaluate the chloride effect using this conventional nebulizer. Data acquisition in the time resolved mode and peak height or peak area measurements were performed by the ICP-MS Chemstation (Hewlett-Packard). A micro-flow nebuliser (PFA-20, CETAC Technologies, Omaha, USA) equipped with quartz capillaries (65 cm length, 50 μm i.d.,) for liquid transport was used in combination with a Scott spray chamber for online chloride interference removal and final arsenic determination. The liquid delivery was supplied by a gas displacement pump (GDP) including a time-programmable flow injection valve (FMS-CETAC, Freudenberg, Germany). The schematic set-up and instrumental parameters applied for this work are summarized in Fig. 1 and and Table I, respectively.

The capillary modification procedure was performed in a capillary electrophoresis system (PrinceCE 560, PrinceCE Technologies, Emmen, The Netherlands) using the regulated flushing of the modification reagents by the instruments pressure control of the instrument.

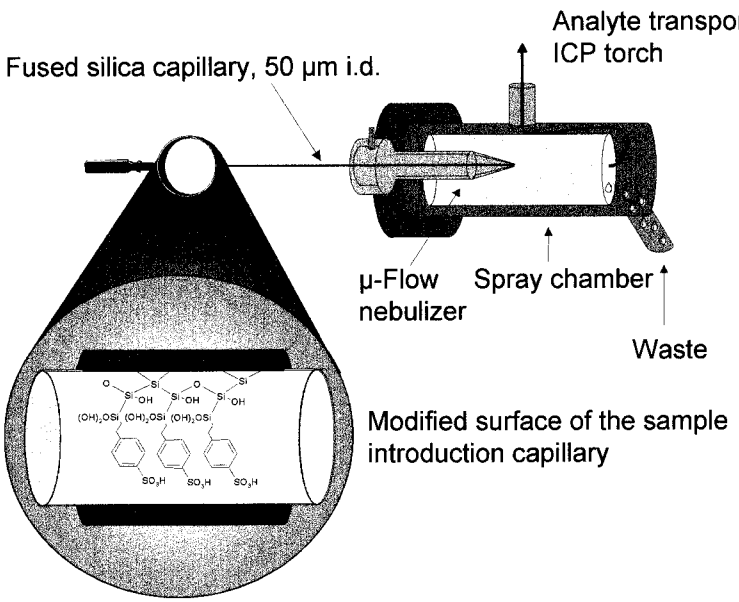

FIGURE 1

TABLE I Working parameters using modified capillary-MCN-ICP-MS

Parameter	*Operating value*
Forward power	1250 W
Sample depth	6.5–7.5 mm
Plasma gas	13.0–15.5 L min^{-1}
Auxillary gas	1.0–1.5 L min^{-1}
Spray chamber temperature	2°C
Nebuliser	Microconcentric
Sample flow rate	20.5 µL min^{-1} (300 psi)
Number of injections	5

Reagents

The capillaries were treated with sodium hydroxide, p.a., methanol (all Merck, Darmstadt, Germany) and 50% (w/w) 3-aminopropyltrimethoxysilane in dichloromethane (ABCR, Karlsruhe, Germany). For ICP-MS analyses stock solution of sodium chloride was prepared by dissolving 10 g of NaCl (Merck, Darmstadt, Germany) in one liter of Milli-Q water (Millipore, Madrid, Spain) and arsenic acid solution (1000 mg L^{-1} 0.5 M HNO_3, Merck) was diluted daily to the working range. Elution was performed with nitric acid, sodium hydroxide and ammonia solution p.a (Merck). Argon ($\geq$ 99.995%, Carburos Metalicos, Spain) as plasma gas was used.

Modification of the Capillary

It is very common in the field of capillary electrophoresis to modify the surface of the capillaries by decreasing or reversing the electrosomotic flow. Various approaches for

the modification of the silica surface using silanizing reagents with the desired functional groups have been reported in the literature. This technique was adapted to our purpose of coating the inner surface of a fused silica capillary with an anionic exchanger material (Fig. 1).

The capillary surface (50 μm i.d. × 360 μm o.d.) (CS-Chromatographie Service, Langerwehe, Germany) was activated with 1 M NaOH. A minimum of 30 min was required for stable modification of the inert surface. Then the capillary was flushed with Milli-Q water (15 min) for the removal of the sodium ions and dried by purging with nitrogen (5 bar) at 80°C for 1 h. After the activation of the capillary surface the anion exchanger was coated on the walls of the capillary by rinsing the capillary with 5% of 3-aminopropyltrimethoxysilane (APTMS) coating reagent in methylene chloride. The capillary was rinsed with this solution for 2 h at a temperature of 60°C with a pressure of 2 bar. The dynamic coating procedure was stopped after every 15 min so that the capillary was coated for 5 min in a static mode. After the coating of the capillary, the reagent not bound to the surface was removed by rinsing the capillary with methylene chloride (20 min) and with water (15 min) at room temperature. Before use the capillaries were purged with nitrogen (5 bar) at 80°C for 2 h.

General Procedure

The instrumental parameters were tuned by both minimizing the $^{156}CeO/^{140}Ce$ signal ratio and optimizing the signal intensity using 10 μg L^{-1} tuning solution of In, Li, Be, Ce and Y with a 500 μL sample loop. The modified capillary was connected to the microconcentric nebuliser and the GDP. Sample solutions of pH 4.5 containing arsenic and chloride at different concentrations were filled into a sample loop (500 μL), then the samples were injected five successive times for 5 s each at a flow-rate of 20.5 μL min^{-1} and the measurements were done in the time resolved mode of the instrument. In the first instance arsenic broke through the capillary while chloride was retained. In order to regenerate the capillary for a new use 10^{-2} M HNO_3 was injected to elute the retained chloride. A standard calibration curve was constructed for the determination of arsenic using APTMS modified capillaries.

RESULTS AND DISCUSSION

In order to evaluate the interference level of chloride on arsenic determination with the instrument employed, experiments were carried out with a conventional Babington type nebuliser connected to the ICP-MS. The results obtained show that chloride at a concentration of 110 mg L^{-1} produced a 21% increase on the analyte signal of 10 μg L^{-1} arsenic (m/z 75) due to both spectroscopic interference and matrix effects. Therefore, it is necessary to develop a methodology to remove this interference.

The various parameters affecting the removal of chloride interference in arsenic determination using modified sample introduction capillaries are: pH of the medium, type of chemical modification of the capillary, flow rate of carrier, sample volume and nature of the eluting solution. All these parameters were optimised to get the best conditions in order to minimise the interference of chloride on arsenic determinations.

Effect of pH

The effect of pH was studied by injecting the most common arsenic species (MMAs, DMAs, inorganic arsenic, AsB and AsC) and chloride solutions at different pH values. The pH was adjusted using dilute solutions of nitric acid and sodium hydroxide. The modified capillary was tested for its interaction with arsenic and chloride injected in the pH range 2–9 (the range in which the modification is stable). As expected the behaviour is strongly dependent on the pH of the sample solution and independent of the arsenic species tested. Figures 2a and b show the effect of pH on arsenic and chloride retention. As a result of the chloride interaction with the surface of the capillaries it was observed that a pH lower than 4 the signal intensity significantly increases with decreasing pH for ^{35}Cl (this fact could be attributed to the competition of NO_3^- and Cl^- for the active sites of the capillary), while in the pH range 4.0–8.0 the signal intensity was almost negligible, presumably above pH 8 the OH^- is occupying all the anionic sites. Arsenic at pH 4.5–5.0 passes through the capillary and there is a very little effect of pH on the signal intensity of arsenic in this pH range. Thus in the pH range selected 4.5–5.0 chloride is retained on the modified surface of the capillary and arsenic breaks through the capillary.

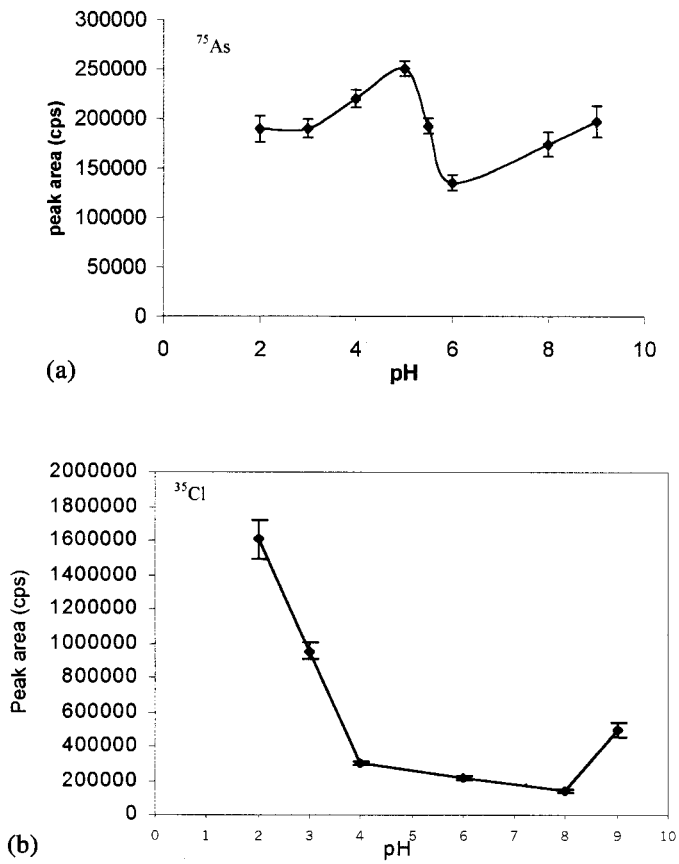

FIGURE 2 Effect of pH on the signal intensity of (a) $10\,\mu g\,L^{-1}$ of arsenate and (b) $20\,\mu g\,L^{-1}$ chloride using AMPTS capillary connected to MCN.

Elution of Chloride

After the arsenic determination it is very important to regenerate the capillary for the next run so the chloride retained in the capillary has to be eluted. Therefore, in order to find the best eluting agent, different eluting solutions such as 10^{-2} M nitric acid, 10^{-5} M sodium hydroxide or 10^{-5} M ammonium hydroxide at pH 9.0 were tested for the elution of chloride. It was observed that 10^{-2} M nitric acid was the best eluent for the chloride retained on the surface of the capillary. Figures 3a and b show the analyte peaks which result after injection of chloride and arsenic. It is observed that chloride is largely retained in the capillary while arsenic breaks through the capillary, and the chloride retained is eluted by several injections of 100 µL of 10^{-2} M nitric acid. Therefore, samples of pH 4.5 and 10^{-2} M nitric acid as eluent were selected for further study. It is important to mention that the whole process including five sample injections, elution and the capillary regeneration can be achieved in about two minutes.

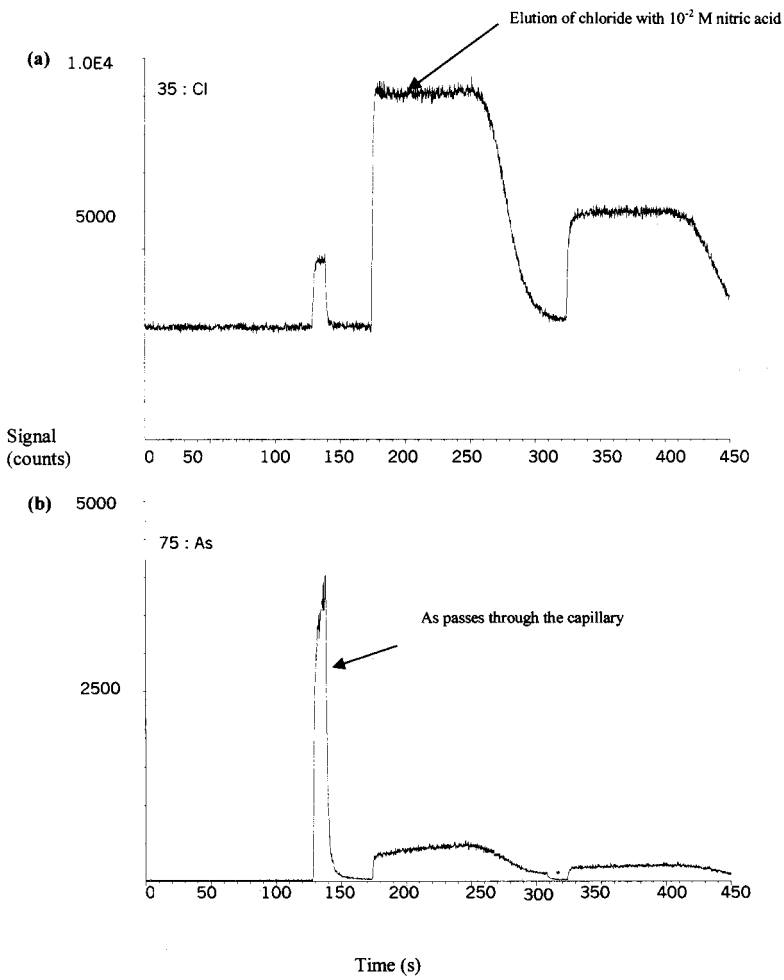

FIGURE 3 Injection of 10 µg L^{-1} of arsenate and 200 µg L^{-1} of chloride and elution of chloride with 10^{-2} M nitric acid using AMPTS capillaries. 5 µL injection volume and 20 µL min^{-1} flow-rate.

Effect of Modification and Retention Capacity of Capillary

The interference level of chloride and the effect of capillary modification were evaluated by comparing the analytical signals with those obtained using a non-modified capillary. The results obtained using a non-modified capillary shown that the presence of 50 mg L^{-1} of chloride produces about 25% signal enhancement of that of 1 μg L^{-1} of arsenic. This increase should not be compared with the results obtained with 10 μg L^{-1} of arsenic using the Babington nebulizer because the set up conditions may be different. However, it can be concluded that the non-modified capillary has not the ability to retain chloride at the mg L^{-1} level.

Working with modified capillaries it was observed that the presence of chloride up to 600 mg L^{-1} did not interfere in the determination of 10 μg L^{-1} of arsenic as shown in Fig. 4. Thus, it can be concluded that the interference removal effect of chloride is due to the use of the chemical modification of the capillary and not to any interaction with the silica capillary surface.

Effect of Sample Injection Volume and Flow Rate

The effect of sample injection volume (evaluated as injection time) was also investigated on the determination of arsenic within the range 2.5–5 μL. It was observed that when sample was injected for 5 s (2.5 μL) the peaks were narrow but when injected for 10 s (5 μL) the peaks were broadened, although the height of the peak did not change significantly. Thus, 5 s was selected for subsequent work.

The effect of flow rate was also evaluated on the retention of chloride. It was observed that at low flow rates within the range 9–20.5 μL min^{-1} chloride was largely retained and did not interfere in the determination of arsenic, while at flow rates higher than 20.5 μL min^{-1} there was a considerable decrease in the retention capacity of the capillary. Therefore, a flow rate of 20.5 μL min^{-1} was selected for further study.

Analytical Characteristics of the Method

Calibration graphs, considering peak area signals, were constructed by injecting 2.5 μL of arsenic solutions in the range 1–180 μg L^{-1} with and without chloride (300 mg L^{-1}) using the MCN connected to the APMTS modified capillary. No significant differences

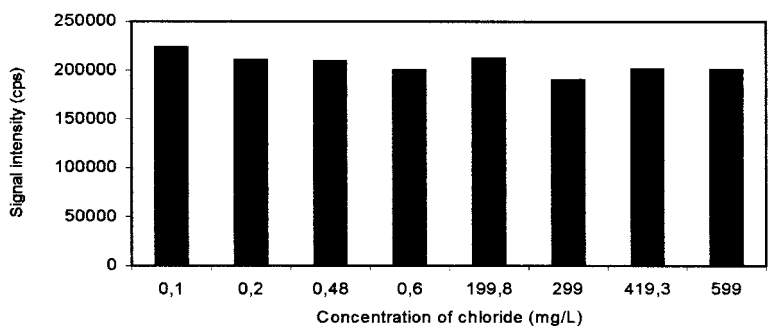

FIGURE 4 Effect of chloride concentration on 10 μg L^{-1} arsenate using AMPTS capillaries for 5 μL injection volume and 20 μL min^{-1} flow rate.

TABLE II Analytical data for arsenic determination in presence of 300 mg L^{-1} of chloride

	^{75}As *Calibration*
Calibration range (μg L^{-1})	1–180
Sensitivity (peak area L ng^{-1})	17.61
Regression coefficient	0.9988
Detection limit (ng L^{-1},3σ)	50
R.S.D. (%) (10 μg L^{-1} of As)	1.5%

between both calibration curves were found at the 95% confidence level. The analytical characteristics of the method are given in Table II.

It was observed that under the optimum working conditions the capillary was not affected when used at least for one month. The modification of the capillary was not destroyed when used in the pH range 2–9.

Applications

The determination of arsenic in urine is very important as a monitor of arsenic exposure. As no urine sample of known composition was available, human urine from two volunteers was collected in glass bottles and stored in a refrigerator until analysis. Because of the high matrix complexity of this kind of sample the effect of dilution required to avoid matrix effect and system damage was carried out. Urine was diluted at different levels (5, 10, 12 and 15 fold) and it was observed that from a 15 times dilution the interferent effect due to chloride was almost negligible because the anion is retained in the capillary. Urine samples were spiked with 10 μg L^{-1} arsenic, diluted 15 times with Milli-Q water and analysed by the proposed procedure. The results of the determination are given in Table III and and indicate that recovery values are quite satisfactory.

The method was applied to the analysis of waste water samples obtained from a collaborative interlaboratory exercise by the M&T programme of the European Commission. The obtained results given in Table III agreed with the average values provided in the individual studies for these samples. This indicates the validity of the applied method. These samples were spiked with arsenic and the recovery values were satisfactory as shown in Table III.

TABLE III Analytical results for the determination of arsenic in human urine and waste water samples

Sample	*Amount of As* (μg L^{-1})			
	Present	*Found*	*Spiked*	*Found*
Human urine (A)	–	–	10.0	12.6 ± 2.0
(B)	–	–	10.0	10.2 ± 1.1
Waste water (A)	37 ± 7	38.6 ± 7.2	20.0	19.5 ± 2.5
(B)	24.8 ± 5.4	26.5 ± 6.4	10.0	9.5 ± 1.3
(C)	9.8 ± 3.45	9.5 ± 3.0	7.0	6.6 ± 0.3

Results are expressed as $\bar{x} \pm s\,(n = 3)$.

CONCLUSIONS

This method of selective retention of interfering element was for the first time applied using 3-aminopropyltrimethoxysilane modified capillaries in order to reduce or eliminate the spectral interference of chloride (as $ArCl^+$) on the determination of arsenic by ICP-MS. The described modification of the inner surface of the silica capillary with anion-exchanger groups could avoid the use of columns for matrix removal, or the tedious application of mathematical models for the correction of interferences and thus could improve and simplify the procedure for ICP-MS analyses. Further the analysis of arsenic in human urine and waste water samples in high chloride concentration matrices increases the utility of this method where a very low amount of sample is required.

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