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Dedicated to Professor Emil Cordoș
on the occasion of his 80th anniversary

DEVELOPMENT AND CHARACTERIZATION OF A METHOD FOR THE DETERMINATION OF TOTAL As IN WATER BY HYDRIDE GENERATION AND OPTICAL EMISSION DETECTION IN ARGON CAPACITIVELY COUPLED PLASMA MICROTORCH

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ABSTRACT. Arsenate was firstly prereduced to arsenite in 0.01 mol L^{-1} HCl (pH 2.00 ± 0.01) and 0.3% L-cysteine, than arsine was generated with 0.5% $NaBH_4$ solution stabilized in 0.5% NaOH and introduced into a capacitively coupled plasma microtorch (10 W, 150 ml min^{-1} Ar) for measurement of As 228.812 nm emission with the Ocean Optics QE65 Pro spectrometer of low resolution. The optimization steps for arsine generation and plasma operation are presented. Under optimal operating conditions, linearity of calibration curve covers the range 0 – 100 μg L^{-1}, while detection and quantification limits are 0.2 and 0.6 μg L^{-1} respectively. Thus, the proposed method is able for As quantification in drinking and groundwater at levels below maximum admitted concentration (10 μg L^{-1}). The method was validated by analyzing certified reference water samples containing 10 – 60 μg L^{-1} As with recovery of 99 ± 6%. (95% confidence level, n = 5 measurements). The analytical capability of the method was demonstrated in the analysis of test samples (drinking-, ground- and waste water) with As concentration in the range 0.6 – 80 μg L^{-1} As with a precision of 1.2 – 10.8%. The completely miniaturized instrument including the capacitively coupled plasma microtorch has analytical potential to be used for monitoring the quality of water sources.

Keywords: *arsenic, hydride generation, water, capacitively coupled plasma microtorch, optical emission spectrometry, miniaturized instrumentation*

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INTRODUCTION

Arsenic is present in environment (water, soil, vegetation) as inorganic (arsenite, arsenate) and organic (monomethylarsonic, dimethylarsinc acid) species, with different toxicity. Thus, inorganic compounds are more toxic and several have been classified as Group I human carcinogens [1,2]. Besides carcinogenicity, exposure of humans to inorganic As species are associated to neurological, cardiovascular and hematological diseases or spontaneous abortion [1,3,4]. One of the sources with high risk of As exposure of population is long-term water consumption at concentrations above or even little below the safety threshold [5–8].

Evaluation of water quality in terms of As concentration and human health risk is of high concern, since more than 500 millions people living in different areas on the Earth like Bangladesh, West Bengal India, Taiwan, Northern Chile, China, Mexico, USA, and Central and Eastern Europe including Romania (700000 people) are chronically exposed *via* water consumption, which is naturally contaminated with arsenic [1,5,8]. In two previous studies, it has been found that soil and groundwater in the vicinity of waste ponds in the Baia Mare area, northern Romania, are polluted with arsenic, in this case as a result of the non-ferrous metal industry very active until 1990 [9,10]. Based on Water Framework Directive (WFD) 2000/60/EC and Groundwater Directive (GWD) 2006/118/EC, European Community established a Maximum Contaminant Level (MCL) of 10 µg L^{-1} As in drinking and groundwater [11–14].

The methods frequently used for As determination in water, foods and beverages are atomic absorption spectrometry in flame/quartz tube with/without hydride generation, electrothermal vaporization atomic absorption spectrometry using different preconcentration procedures to enhance sensitivity [15 – 20], molecular absorption spectrophotometry [21] or fluorescent spectroscopy based on ultra-small ZnO particles [22]. In addition, coupling a separation technique like high performance liquid chromatography with inductively coupled plasma mass spectrometry provides speciation of different As compounds [23]. Recent advances in spectrometric methods to enhance sensitivity for the determination of elements, including total As or its speciation, after chemical vapor/ hydride generation (HG), were reviewed by several authors [24–28]. A green derivatization approach based on UV photo-induced hydride generation in the presence of formic or acetic acid was successfully applied for the determination of As in surface water prior measurements by atomic fluorescence spectrometry or other spectrometric methods [29,30]. A new generation of miniaturized UV-Vis spectrometric systems which valorize microplasmas technology able to be interfaced with a microspectrometer, was successfully tested for the determination of elements (Hg, As, Sb, Se and transitional metals) forming chemical vapor *via* classical or sono-/UV induced procedure [31–37]. In our laboratory it was recently developed a method for As and Sb determination in non- and biodegradable materials and soil by hydride generation capacitively coupled plasma microtorch optical emission spectrometry (HG-µCCP-OES) [38,39].

The aim of the study was to evaluate whether the HG-µCCP-OES method, which involves arsine generation from As(III) species in the presence of $NaBH_4$ in diluted HCl solution and L-cysteine, is suitable for the determination of total As in various water types. The method was optimized and characterized in terms of linearity, limit of detection and quantification, accuracy and precision. The analytical capability of the proposed method was demonstrated by analyzing samples of drinking water, groundwater and waste water with different As concentration. The novelty of the study lies in the fact that the method has been implemented for the first time on a miniaturized prototype model, which provides benefits related to low consumption of energy and argon for plasma generation and reduction of used reagents.

RESULTS AND DISCUSSION

Optimization of the working conditions for As determination in water by HG-µCCP-OES

The HG-µCCP-OES method was optimized in terms of general conditions for hydride generation (concentrations of HCl, L-cysteine, $NaBH_4$ and NaOH) and plasma operation (power, Ar flow rate). The optimization criterion was to get the highest emission signal at As 228.812 nm. The influence of conditions for arsine generation from As(III) species on emission signal is presented in Figures 1-4.

The examination of Figures 1–4 evidentiated the following optimal conditions in terms of reagent concentrations for arsine generation from As(III) species: 0.01 mol L^{-1} HCl in sample and carrier (pH 2.00±0.01); 0.3% L-cysteine in sample; 0.5% $NaBH_4$ stabilized in 0.5% NaOH.

The optimal conditions for plasma operation were previously found to be 10 W plasma power and 150 mL min^{-1} Ar for arsine purge and plasma sustaining, and 0 mm observation height [39].

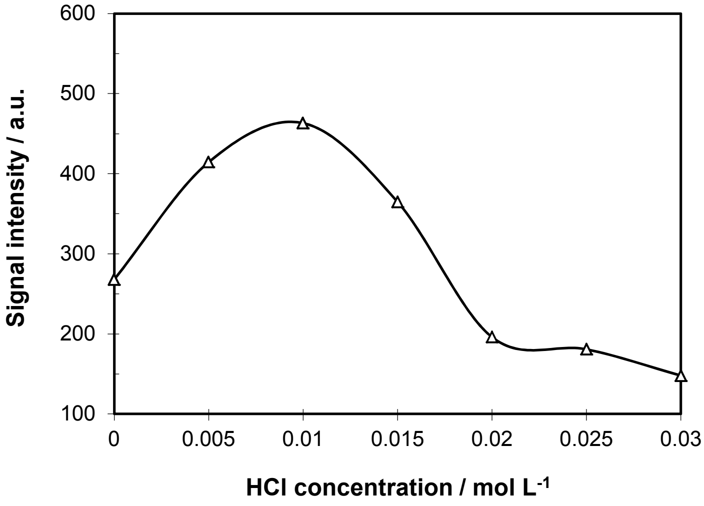

Figure 1. Influence of HCl concentration in sample on As 228.812 nm emission signal after arsine generation from As(III) species. Experimental conditions: 50 µg L^{-1} As; identical concentration of HCl in sample and carrier; 0.3% L-cysteine; 0.5% $NaBH_4$ stabilized in 0.5% NaOH; 10 W plasma power; 150 mL min^{-1} Ar as gas for arsine purge and plasma sustaining

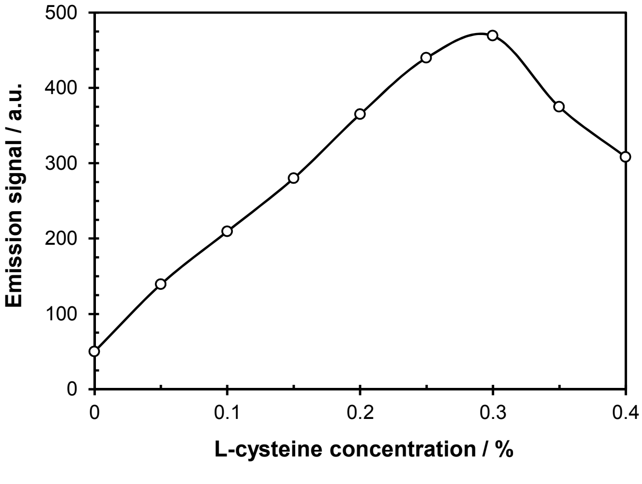

Figure 2. Influence of L-cysteine concentration in water sample on As 228.812 nm emission signal after arsine generation from As(III) species. Experimental conditions: 50 µg L^{-1} As; 0.01 mol L^{-1} HCl in sample and carrier; 0.5% $NaBH_4$ stabilized in 0.5% NaOH; 10 W plasma power; 150 mL min^{-1} Ar as gas for arsine purge and plasma sustaining

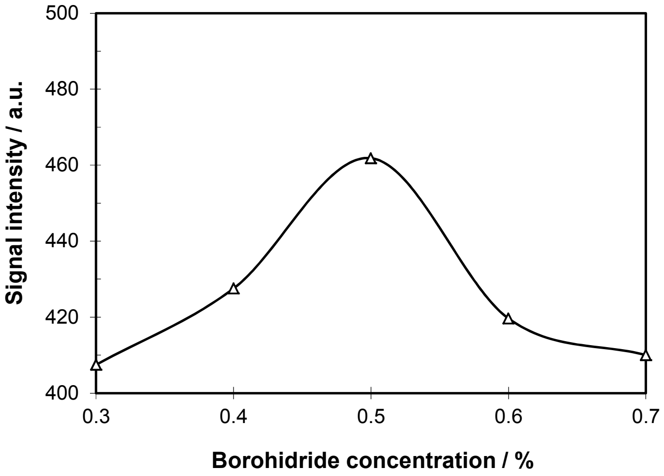

Figure 3. Influence of $NaBH_4$ concentration in hydride generation reagent on As 228.812 nm emission signal after arsine generation from As(**III**) species. Experimental conditions: 50 μg L^{-1} As; 0.01 mol L^{-1} HCl in sample and carrier; $NaBH_4$ solution stabilized in 0.5% NaOH; 10 W plasma power; 150 mL min^{-1} Ar as gas for arsine purge and plasma sustaining

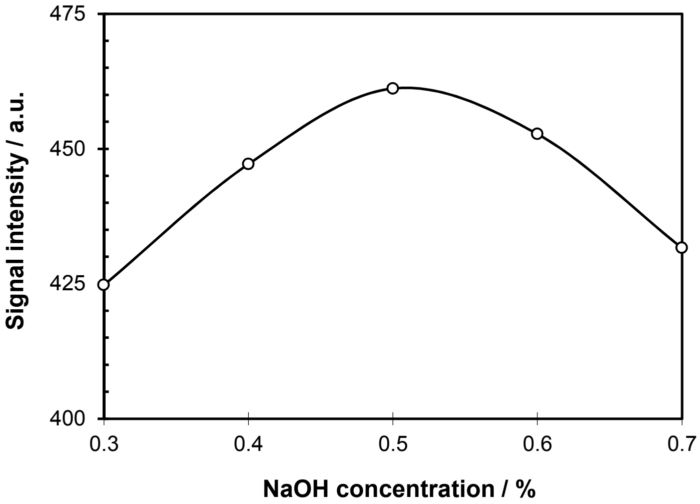

Figure 4. Influence of NaOH concentration in hydride generation reagent on As 228.812 nm emission signal after arsine generation from As(**III**) species. Experimental conditions: 50 μg L^{-1} As; 0.01 mol L^{-1} HCl in sample and carrier; 0.5% $NaBH_4$; 10 W plasma power; 150 mL min^{-1} Ar as gas for arsine purge and plasma sustaining

Figures of merit for As determination in water by HG-μCCP-OES

The HG-μCCP-OES method was assessed regarding linearity of the calibration curve, limit of detection and quantification, and accuracy. The limit of detection was calculated using the 3σ criterion from the parameters of the calibration curve ($3s_{y/x}/m$), where ($s_{y/x}$) was the standard deviation of residuals (3.4795) and (m) the calibration sensitivity (8.8917) over the range 0 – 100 μg L^{-1} As(III) in standards. Limit of quantification was considered to be 3 folds the limit of detection. The parameters of the calibration curve for As are presented in Fig. 5.

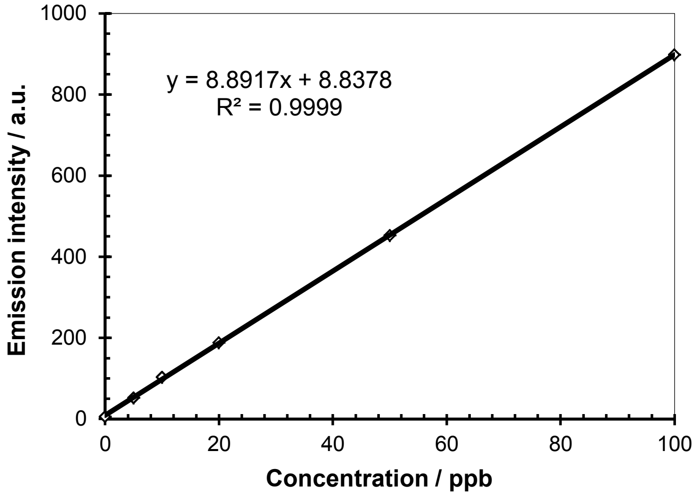

Figure 5. Calibration plot for As 228.812 nm in HG-μCCP-OES over the range 0 – 100 μg L^{-1} As

The limit of detection by HG-μCCP-OES was 0.2 μg L^{-1} and limit of quantification of 0.6 μg L^{-1}, above which As quantification in water is achievable. The limit of detection is 50 folds lower than the maximum concentration limit in drinking water and groundwater according to current guidelines [13,14,40] so that the HG-μCCP-OES method fulfils the demands for such kind of analysis.

Arsenic concentrations found in certified reference water samples by HG-μCCP-OES are presented in Table 1.

Data in Table 1 demonstrate that the HG-μCCP-OES method provides a good accuracy for As determination in drinking water and groundwater with recovery in the range 99±6%. No significant differences were between certified and found concentrations.

Table 1. Results (μg L^{-1}) obtained for As determination in certified reference samples of water by HG-μCCP-OES.

Certified sample	Type	Certified value±U	Found value±U [a]	Recovery/%[b]
LGC 6010	Drinking water	55±5	54±3	98±6
ERM-CA011b	Drinking water	10.15±0.34	10.25±0.85	101±8
SRM 1643e	Synthetic	60.45±0.72	60.55±0.72	100±1
ERM-CA615	Groundwater	9.9±0.7	10.0±0.5	101±5
BCR 610	Groundwater	10.8±0.4	10.5±0.5	97±5

[a] – Expanded uncertainty for 95% confidence level and (n=5 parallel measurements)
[b] – Recovery for 95% confidence level and (n=5 parallel measurements)

Analysis of test samples of water

The total As concentration found in several real samples of water are provided in Table 2.

Table 2. Total As in water samples by HG-μCCP-OES

Sample	Sample size	As/μg L^{-1}				RSD/%[a]
		Min	Max	Mean	Median	
Drinking water[b]	9	0.6	2.8	1.9	2.1	5.0 – 10.8
Non-contaminated groundwater[c]	13	3.2	9.1	5.8	5.4	1.8 – 8.0
Contaminated groundwater[c]	18	10.9	79.9	32.6	27.5	1.2 – 7.1
Waste water[d]	6	12.8	25.2	17.2	17.1	1.6 – 9.3

[a] – RSD - relative standard deviation (n = 5)
[b] – collected from private wells and water supply network
[c] – collected from western and south-western Romania (natural enrichment)
[d] – contaminated water (no treatment) from mining and non-ferrous metal industry

Data in Table 2 confirm that the HG-μCCP-OES method can be used for accurate determination of As in water of different origin. For concentrations in the range 0.6 – 80 μg L^{-1} precision of repeated measurements (n = 5) was between 1.2 – 10.8%.

CONCLUSIONS

It was developed and characterized a method for As determination in different types of water after hydride generation using a prototype system based on a capacitively coupled plasma microtorch coupled with a low resolution microspectrometer for optical emission measurements. The proposed method developed on fully miniaturized instrumentation fulfils the required analytical performances for As determination in water at concentrations level much below that maximum admitted in drinking and groundwater. Under these circumstances the HG-µCCP-OES prototype system has promising perspectives to be used for monitoring As in diverse water sources.

EXPERIMENTAL SECTION

Reagents, standard solutions, CRMs and water test samples

Hydrochloric acid, 30% (m/m), ultrapur (< 5 ng L^{-1} As), $NaBH_4$ pro analysis (< 0.001% As), NaOH suprapur (99.99%), L-cysteine for biochemistry (< 0.0005% As), stock solution of As(V) 1000 µg mL^{-1} were purchased from Merck (Darmstadt, Germany). A solution of 3% L-cysteine in HCl (pH = 2.00±0.01) was used to prereduce As(V) to As(III), while a solution of 0.01 mol L^{-1} HCl (pH = 2.00±0.01) was used as carrier. The solution of 0.3% L-cysteine in HCl (pH = 2.00±0.01) was used as carrier of arsine into plasma. The solution of 0.5% $NaBH_4$ stabilized in 0.5% NaOH used as derivatization reagent was daily prepared. Calibration of HG-µCCP-OES was carried out with standards in the range 0 – 100 µg L^{-1} As after prereduction in the presence of 0.3% L-cysteine in HCl medium (pH 2.00±0.01) on water bath for 10 min. The HG-µCCP-OES method was assessed for by analyzing several certified reference materials of water (ERM CA011b Hard Drinking Water UK - Metals, LGC 6010 Hard Drinking Water, ERM-CA615 Groundwater, BCR 610 Groundwater, SRM 1643e Trace Elements in Water) acquired from LGC Promochem (Wesel, Germany). The applicability of the method was checked on real samples of drinking water, groundwater and waste water with As content below or above the maximum concentration level in drinking water.

The glassware was soaked in 5 mol L^{-1} HNO_3 for 12 h and rinsed with Milli-Q water.

Water sample preparation for As determination by HG-µCCP-OES

Determination of As in water samples in the presence of L-cysteine in dilute HCl solution involves two steps: (i) prereduction of As(V) to As(III) and (ii) arsine generation from As(III). After filtration, an aliquot volume of 10 – 40 mL sample was mixed with 5 ml 3% L-cysteine in 0.01 mol L^{-1} HCl and heated on water bath at 90±5 ºC for 10 min for prereduction of As(V). After cooling, pH was adjusted to (2.00±0.01) by potentiometric titration and diluted to 50 mL with HCl solution of (2.00±0.01) pH. In this way water samples had a final concentration of 0.3% L-cysteine and (2.00±0.01) pH. The samples of CRMs and calibration standards of As were prepared in the same way.

Operation of the HG-μCCP-OES equipments

The HG-μCCP-OES equipment is a miniaturized prototype consisting of a plasma microtorch (INCDO-INOE 2000 Bucharest, Research Institute for Analytical Instrumentation, Cluj-Napoca, Romania), a free-running generator (13.56 MHz, 10 – 30 W, 15x17x24 cm^3 size) (Technical University Cluj-Napoca, Romania), a HGX-200 hydride generator (Omaha, Nebraska, USA) and a QE65 Pro Spectrometer (190 – 380 nm, 3648-element Toshiba CCD-array detector, 0.4 nm FHWM), (Ocean Optics, Dunedin, USA). Constructive and operation details are presented in Table 3.

Table 3. Constructive details and working conditions for the HG-μCCP-OES prototype equipment

Component	Description
Plasma microtorch	Capacitively coupled with Mo tip microelectrode of 1 mm diameter (Goodfellow, Cambridge, UK), quartz tube of 160 nm cut-off, 5 mm i.d., 25 mm length (H. Baumbach & Co. Ltd., Ipswich Suffolk, UK); Ar and arsine intake into plasma through channels of 0.75 mm; other constructive details are available in ref. [38]; 10 W plasma power; 150 mL min^{-1} Ar flow for arsine purging from hydride generator and plasma sustaining; 0 mm viewing height.
Radiofrequency generator	Free running, 10 - 30 W, 13.56 MHz (Technical University, Cluj Napoca, Romania).
Hydride generator	HGX-200 CETAC (Nebraska, USA). Flow rates: sample 7 mL min^{-1}; $NaBH_4$ solution 1 mL min^{-1}; carrier (HCl solution, pH 2.00±0.01) 1 mL min^{-1}, MasterFlex L/S peristaltic pump with 4-channels (Model 7535-04, Cole Parmer, Montreal, Canada).
Spectrometer	QE65 Pro Ocean Optics (Dunedin, USA), 190 – 380 nm spectral range; 0.4 nm FWHM, Toshiba CCD detector with 3648 pixels cooled at (– 20 ºC) with Peltier element, back-illuminated.
Signal processing	Spectrasuite software, peak height signal at As 228.812 nm, 10 s integration time, background correction using two points model.

Measurement of As emission by HG-µCCP-OES was carried out as follows: 1. registration of plasma background during pumping of 0.3% L-cysteine in HCl solution with pH (2.00±0.01) as blank; 2. background correction; 3. registration of the net spectrum containing the As 228.812 nm emission signal after aspirating standards/CRMs/test water samples in the HGX-200 generator. Memory effects were overcome by washing the sample channel of the generator with the following solution to be measured for 40 s. The emission spectrum of As in HG-µCCP-OES was already presented [38,39].

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