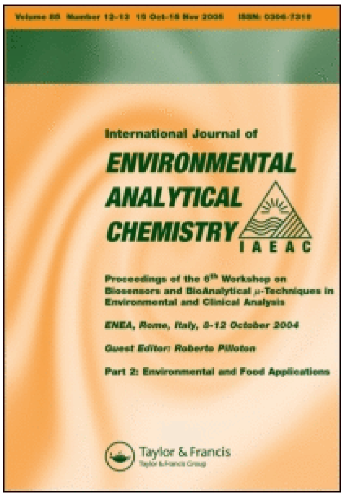

International Journal of Environmental Analytical Chemistry
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713640455

Comparison of voltammetric and AAS methods for As(III) quantification in presence of iron species in model water samples with a low mineral content

Virginie Pallier[a]; Bernard Serpaud[a]; Geneviève Feuillade-Cathalifaud[b]; Jean-Claude Bollinger[a]
[a] Groupement de Recherche Eau Sol Environnement (GRESE), Université de Limoges, Faculté des Sciences et Techniques, 123 Avenue Albert Thomas 87060 Limoges, France [b] Groupement de Recherche Eau Sol Environnement (GRESE), Université de Limoges, ENSIL, Parc d'Ester Technopôle, 16 rue Atlantis 87068 Limoges, France

To cite this Article Pallier, Virginie , Serpaud, Bernard , Feuillade-Cathalifaud, Geneviève and Bollinger, Jean-Claude(2011) 'Comparison of voltammetric and AAS methods for As(III) quantification in presence of iron species in model water samples with a low mineral content', International Journal of Environmental Analytical Chemistry, 91: 1, 1 — 16
To link to this Article: DOI: 10.1080/03067310902977534
URL: http://dx.doi.org/10.1080/03067310902977534

Intern. J. Environ. Anal. Chem.
Vol. 91, No. 1, 15 January 2011, 1–16

Comparison of voltammetric and AAS methods for As(III) quantification in presence of iron species in model water samples with a low mineral content

Virginie Pallier[a], Bernard Serpaud[a], Geneviève Feuillade-Cathalifaud[b]* and Jean-Claude Bollinger[a]

[a]*Groupement de Recherche Eau Sol Environnement (GRESE), Université de Limoges, Faculté des Sciences et Techniques, 123 Avenue Albert Thomas 87060 Limoges, France;* [b]*Groupement de Recherche Eau Sol Environnement (GRESE), Université de Limoges, ENSIL, Parc d'Ester Technopôle, 16 rue Atlantis 87068 Limoges, France*

(*Received 24 November 2008; final version received 17 April 2009*)

Voltammetry was adapted to quantify As(III) in model water samples with a low mineral content and compared to the Hydride Generation Atomic Absorption Spectrometry (HG-AAS) method. The specificity lies in the study of the influence of interfering species on the quantification of samples treated by coagulation/flocculation using iron salts. First, a Square Wave Cathodic Stripping Voltammetry method at a Hanging Mercury Drop Electrode (SW-CSV – HMDE) was optimised and compared with the HG-AAS method. Second, the influence of the presence of Fe(II), Fe(III) and As(V) was evaluated. No interferences from As(V) were observed, however for both methods, the As(III) signal decreased by 10% in presence of iron. Standard addition method was thus required to efficiently quantify As(III) in complex matrix and the SW-CSV (limit of quantification $= 0.5\,\mu g\,L^{-1}$) method was preferred to the HG-AAS technique to determine low As(III) levels ($[As(III)] \leq 2\,\mu g\,L^{-1}$).

Keywords: arsenite; SW-CSV; HG-AAS; iron interferences

1. Introduction

Arsenic is widespread in the environment because of numerous natural sources [1] and anthropogenic activities [2]. Its concentration can reach high values in surface and groundwaters by leaching from the source rocks and soils [3]. High concentrations in drinking water can cause serious damage on human health [4] and the important chronic arsenic toxicity has caused many regulating agencies (WHO, US-EPA) to reduce its maximum contaminant level in drinking water to $10\,\mu g\,L^{-1}$. In this way and because of the more important toxicity of inorganic arsenic compounds [1] with a predominant presence of the trivalent and pentavalent oxidation states in natural water samples [5], the development of ultra-trace analytical methods is required, allowing in addition the differentiation between As(III) and As(V).

---

*Corresponding author. Email: feuillade@ensil.unilim.fr

ISSN 0306–7319 print/ISSN 1029–0397 online

DOI: 10.1080/03067310902977534
http://www.informaworld.com

Many authors have tried to develop and optimise methods for the determination of trace levels of arsenic. Electrochemical techniques have been demonstrated to be low cost, sensitive and accurate methods to quantify very low amounts of arsenic in natural water samples. Among them, stripping voltammetry is widely used because of the preconcentration of the substance to quantify on the working electrode [6]. Anodic stripping voltammetry methods were developed, with a gold working electrode instead of a mercury electrode because of the interferences related to the oxidation of mercury [7–10]. However, problems associated with As(V) at solid electrodes (memory effects, limited sensitivity, poor precision, interference with copper) make this method inconvenient for routine analysis [11–12]. Thus, we paid attention to the use of cathodic stripping voltammetry, especially Square Wave Cathodic Stripping Voltammetry (SW-CSV). This method is more sensitive and faster than either linear scan or differential pulse, with a mercury working electrode. This electrode is widely used and does not present the disadvantages of solid electrodes for which the response depends on past history and for which oxide films can be formed [13]. The quantification of arsenic by CSV requires a strong acidic medium to allow the reduction of As(III) to the element [12]. Then, the second step corresponds to the reduction of As(0) to arsine. During this step, arsenic, as an intermetallic compound, is preconcentrated on the mercury electrode by plating at the required potential and then scanning the voltage in the cathodic direction to obtain a peak due to the formation of arsine $AsH_{3(g)}$ [13].

Hydride Generation Atomic Absorption Spectrometry (HG-AAS) is one of the analytical methods that have been developed for the determination of arsenic at trace levels. This relatively fast and sensitive technique is based, as the voltammetric method, on the determination of As(III) after its reduction to arsine in acidic medium. After several optimisations, the obtained detection limit varies between 0.1 and $0.4\,\mu g\,L^{-1}$ [14–15].

The aim of this study was to adapt and to compare two analytical laboratory methods, an optimised SW-CSV method and a HG-AAS method to quantify low levels of As(III) ($[As(III)] \leq 10\,\mu g\,L^{-1}$) in model water with low mineral content after arsenic treatment by coagulation/flocculation. Higher concentrations have not been considered because HG-AAS is known to be accurate and repeatable for $[As(III)] > 10\,\mu g\,L^{-1}$. This model water has a composition similar to some natural groundwaters and its use for validating the methods allowed working on a medium with a given and constant composition and thus controlling all the parameters (matrix composition and As concentration). As a consequence, the identification of the specific interferences on the analytical procedures is easier because the As(III) concentration was controlled while day-to-day variations in As level and speciation in environmental samples may be important [16]. These interferences on the polarographic and spectrometric As(III) determinations have already been studied by several authors but the use of coagulation/flocculation [17–20] to remove arsenic for drinking water production requires reconsideration and revaluation. Thus, because of the efficiency of iron salts compared to aluminium ones [17,21,22], particular attention was paid to their behaviour and influence on the signal response. The influence of As(V) was also studied because of the possible oxidation of As(III) in samples matrix conditions and because As(V) and As(III) can coexist in natural water samples. This study only deals with the quantification of As(III). However, the analysis of natural water samples involved the determination of total arsenic concentrations. Graphite furnace atomic absorption spectrometry was used for the quantification of total arsenic and As(V) was obtained by difference between total arsenic concentrations and As(III) concentrations.

2. Experimental

All the glassware and polyethylene bottles used for the preparation of the solutions, the storage and the analysis of the samples were cleaned, stored in 10% (v/v) HNO_3 for at least two days and then rinsed 6 times with ultrapure grade water.

2.1 *Apparatus*

All voltammetric measurements were done under potentiostatic control (μAutolab PSTAT 10 controlled by GPES software from Eco Chemie) using a Metrohm stand 663 equipped with a standard three-electrodes cell with a hanging mercury drop working electrode, a platinum wire auxiliary electrode and an Ag/AgCl/3 M KCl/1 M KCl reference electrode. The temperature was kept constant at $20 \pm 1°C$. A central stirrer and a N_2 (purity $\geq 99.995\%$) purge tube were used for stirring the solution during the deposition step and removing the oxygen dissolved in the solution.

A Varian SpectrAA 220 Flame atomic absorption spectrometer equipped with a Varian VGA-77 (Vapour Generation Assembly) for the hydride generation was used for As(III) measurements. The working conditions as optimised [23] allow the quantification limit of $0.6\,\mu g\,L^{-1}$ to be achieved.

2.2 *Reagents and chemicals*

All the reagents used were of the purest grade available and the solutions were prepared in ultrapure grade water (Milli-Q system: resistivity 18.2 MΩ.cm, TOC $< 10\,\mu g\,L^{-1}$). Concentrated HCl (Fluka, 32%, $\rho = 1.16$ kg/L) was specific for arsenic determination. The As(III) stock solution ($1000\,mg\,L^{-1}$) was prepared by dissolving the appropriate amount of $NaAsO_2$ (Fluka) in ultrapure grade water. This solution was stored at 4°C during one month and the required solutions for the voltammetric optimisations and analysis were prepared daily by dilution. The Cu(II) standard solution ($5000\,mg\,L^{-1}$) was prepared by dissolving $CuCl_2 \cdot 2H_2O$ (Merck, As $\leq 0.0001\%$ and Fe $\leq 0.001\%$) in 0.1% HCl (v/v). The 0.1% (w/v) sodium borohydride and 3.5% (w/v) citric acid reagents used for the HG-AAS determinations were prepared daily by dilution of the appropriate amount of $C_6H_8O_7$ (Fluka, As $\leq 0.00001\%$, Fe $\leq 0.0005\%$, assay $\geq 99.5\%$) and $NaBH_4$ (Merck, As $\leq 0.001\%$, Fe $\leq 0.005\%$) in 0.2% (w/v) NaOH (Merck, Fe $\leq 0.0005\%$).

For the study of the interferences on the As(III) determination, the As(V) stock solution was prepared by dissolving $Na_2HAsO_4 \cdot 7H_2O$ (Fluka) in ultrapure grade water and this solution was stored for one month at 4°C. The Fe(II) and Fe(III) stock solutions were prepared daily from $Fe(NH_4)_2(SO_4)_2 \cdot 6H_2O$ (Fluka) and $FeCl_3 \cdot 6H_2O$ (Riedel-deHaën, As $\leq 0.0005\%$), respectively. These studies of the As(V), Fe(II) and Fe(III) interferences on the As(III) determination were done by addition of increasing amounts of the stock solutions.

2.3 *Model water*

The model water composition (Table 1) is based on an original compilation [24] of 23 groundwaters from a granitic area used to produce drinking water. It is doped with As(III) concentrations from 0.5 to $10\,\mu g\,L^{-1}$ in order to evaluate the linearity of the method and

Table 1. Characteristics of the model water (major species concentrations and chemical parameters) (from Ref. [24]).

	Total concentrations	
	mmol L^{-1}	mg L^{-1}
Calcium	0.0798	3.2
Magnesium	0.0535	1.3
Sodium	0.3000	6.9
Potassium	0.0205	0.8
Sulfate	0.0355	3.4
Chloride	0.2273	8.1
Nitrate	0.1597	9.9
Silica	0.1500	9.0
pH	6.0 ± 0.1	
Alkalinity (mgCaCO$_3$ L^{-1})	9 ± 2	

the possible interferences of the matrix composition on the SW-CSV and HG-AAS analysis.

To study the influence of NOM on As(III) quantification by SW-CSV and HG-AAS, the model water was spiked with humic substances. Humic acid (sodium salt from Aldrich) solution was filtered on 0.45 μm to remove humins. The NOM solution was thus a mixture of humic acids (75%) and fulvic acids (7%).

2.4 *Voltammetric procedure for As(III) determination*

For the voltammetric determination of As(III), the Square Wave Cathodic Stripping Voltammetry with a Hanging Mercury Drop Electrode (SW-CSV – HMDE) was used. 16 mL of sample, 4 mL of 32% HCl (final concentration = 2 M) and 100 μL of 5000 mg L^{-1} Cu(II) solution (final concentration = 25 mg L^{-1}) were introduced into the polarographic cell. The analyses were performed with the standard additions method, under the instrumental conditions optimised and presented in Table 2. Four consecutive additions of small volumes (between 20 and 100 μL) from a known As(III) solution were made to the polarographic cell.

All these experiments were carried out in the polarographic cell previously purged with nitrogen gas (purity $> 99.995\%$) during 10 min; 60 s of purge was applied after cell opening and 20 s before each scan. Besides, each scan was repeated three times to ensure of the repeatability of the method by measuring the peak current.

2.5 *The HG-AAS procedure*

The spectrometric HG-AAS method used for the determination of As(III) was previously applied by Michon [23]. As(III) is reduced to arsine in acidic medium, with a 0.1% (w/v) sodium borohydride reducing agent solution in 0.2% w/v NaOH. The pH was optimised and fixed between 2.5 and 3.5 by using a 3.5% (w/v) citric acid solution. These optimised parameters allowed the specific determination of As(III) without any interference caused

Table 2. Initial and final optimised electrochemical and chemical parameters for the determination of As(III) by SW-CSV.

	Initial parameters	Optimised parameters
Chemical parameters		
HCl concentration	$1\,\text{mol}\,L^{-1}$	$2\,\text{mol}\,L^{-1}$
Cu(II) concentration	$25\,\text{mg}\,L^{-1}$	$25\,\text{mg}\,L^{-1}$
Electrochemical parameters		
Purge time	20 s	20 s
Deposition potential	−0.43 V	−0.41 V
Deposition time	50 s	60 s
Equilibration time	10 s	10 s
Frequency	50 Hz	50 Hz
Initial potential	−0.6 V	−0.6 V
End potential	−1.0 V	−1.0 V
Step potential	2 mV	2 mV
Amplitude	52 mV	52 mV

by the presence of [As(V)] $<200\,\mu g\,L^{-1}$. The study of the influence of other species underlined the necessity to use the standard addition method for the quantification with the same procedure as described above.

3. Results and discussion

3.1 *Working up the SW-CSV – HMDE method*

The principle for the analytical procedure is to preconcentrate arsenic in the presence of copper at a mercury drop electrode by controlled potential electrolysis and subsequently to strip the arsenic by applying a cathodic potential scan, whereby the arsenic is further reduced to As(-III) [25]. These reactions are possible in acidic medium and an optimisation of the electrochemical parameters and supporting electrolyte composition was required: specially deposition potential E_{dep}, deposition time T_{dep}, acid and Cu(II) concentrations, because they have an influence on the peak shape and intensity and because results available in the literature on this topic are very versatile.

3.1.1 *Optimisation of the voltammetric parameters and supporting electrolyte conditions*

The voltammetric parameters (deposition potential and time) were first optimised by introducing, as the supporting electrolyte, 18 mL of ultrapure grade water, 2 mL of 32% HCl (final concentration 1 M) and 100 μL of $5000\,\text{mg}\,L^{-1}$ Cu(II) solution (final concentration $25\,\text{mg}\,L^{-1}$). These supporting electrolyte conditions were chosen according to literature [11–12]. A 20 s purge was applied after varying the parameter. In these conditions, highest peak intensities combined with symmetrical peak shape were obtained for $E_{dep} = -0.43\,V$ and $T_{dep} = 50\,s$ for [As(III)] $<10\,\mu g\,L^{-1}$. The other initial electrochemical parameters for SW-CSV, as reported in Table 2, were defined according to the data found in the literature and previous tests. After having optimised these two electrochemical parameters, the effect of the HCl and Cu(II) concentrations on the As(III) peak intensity was tested. A modification of the supporting electrolyte composition would involve checking the deposition potential and time already optimised.

3.1.1.1 *Effect of acid concentration.* Determination of arsenic in the presence of Cu(II) ions requires an acidic medium to ensure the reduction of As(III) and Cu(II) to the corresponding element [12]. According to literature, voltammetric arsenic detection is possible in HCl [11,12,26–29], HBr [30], HNO_3, H_2SO_4 and $HClO_4$ [31]. HCl is the most widely used acid, although detection limits as low as 10 ng As(III) L^{-1} and 20 ng As(V) L^{-1}, better As(III) peak and hydrogen catalytic wave separation, increased reproducibility and more stable baseline were claimed in HBr medium [30]. By using the initial voltammetric parameters (Table 2), the influence of HCl concentration was tested for $1\,M \leq HCl \leq 5\,M$ and $Cu(II) = 5$, 25 and 50 mg L^{-1}. Highest peak intensities and lowest background currents were obtained for 2 M HCl and 25 mg L^{-1} Cu(II). Indeed, in these conditions, the ratio ‘Peak intensity/Background current’ was the highest and the sensitivity increased consequently. For 1 M HCl, only the Cu(II) concentration of 25 mg L^{-1} allowed detecting 1 µg As(III) L^{-1}, but the peak intensity was reduced by around 60% in comparison with the peak obtained in 2 M HCl and 25 mg L^{-1} Cu(II). For higher HCl concentrations (3, 4 and 5 M), a 5 mg L^{-1} Cu(II) concentration was insufficient to detect a low amount of As(III). With 25 mg L^{-1} Cu(II), the peak intensity decreased with HCl concentration. On the contrary, with 50 mg L^{-1} Cu(II), it increased but peaks presented a shoulder and the background current was important like in previous studies where As(III) quantifications were performed in presence of 50 mg Cu(II) L^{-1} and 40 µM $N_2H_4 \cdot H_2SO_4$ to stabilise the peak current [26] or by using a hanging copper amalgam drop electrode as working electrode [28]. These results emphasised that 2 M HCl was the optimal HCl concentration for As(III) determination by SW-CSV because it allowed achieving lower detection limit by combination of high peak intensity and low background current. According to Li and Smart [26], such a high acid concentration favours the reduction of both As(III) and Cu(II).

3.1.1.2 *Effect of Cu(II) concentration.* Arsenic cannot be preconcentrated directly at the mercury electrode because of its low solubility [11]. Thus, the formation of an intermetallic compound is required, either with copper [11,12,26,29,30], a mixture of selenium and copper [27] or a mixture of copper and sodium diethyldithiocarbamate [31]. Copper is the most widely used and Cu(II) concentration plays a decisive role in the accumulation process. According to literature, several Cu(II) concentrations have already been tested [11,12,26,29,30] but none of them appears to be the best.

The optimisation of Cu(II) concentration in the supporting electrolyte was performed in 2 M HCl and with a 60 s purge time between each Cu(II) solution addition. Several Cu(II) concentrations from 5 to 50 mg L^{-1} were tested and the influence of these concentrations on peak intensity and background current was evaluated (Figure 1). Higher Cu(II) concentrations were not tested because it has been demonstrated previously that for $[Cu(II)] > 60$ mg L^{-1} and $HCl = 1\,M$, the maximum peak intensity decreases [12] or, on the contrary, by using 0.45 M HBr in the electrolyte support, the peak height increases but peaks are larger and less repeatable [30].

The required Cu(II) concentration in the supporting electrolyte depends on the amount of As(III) to be quantified and on the deposition time applied. Indeed, for low Cu(II) concentrations, the maximum As(III) peak current is reached for a longer deposition time

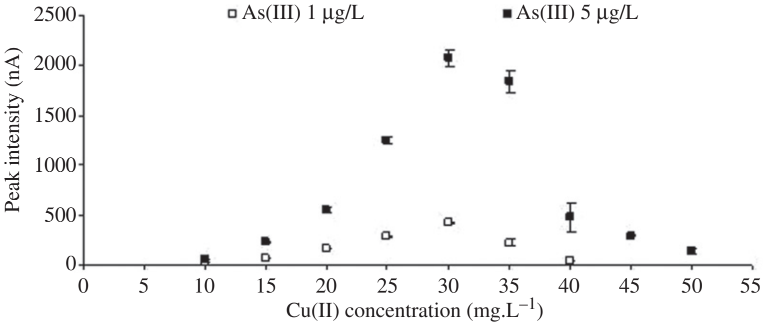

Figure 1. Evolution of As(III) peak intensity as a function of Cu(II) concentration in 2 M HCl (E_{dep} −0.43 V, T_{dep} 50 s) – Error bars for $n = 3$.

[11,12,26,31] and we showed that lower As(III) concentrations required a minimum Cu(II) concentration to be detected (Figure 1). In this study, the deposition time was fixed and maximum peak current was reached by increasing the amount of Cu(II) in the supporting electrolyte until 30 mg L^{-1}. However, such a Cu(II) concentration led to an important background current involving less sensitivity and accuracy in the measurements. For higher Cu(II) concentrations, the peak current declined and even disappeared for [Cu(II)] ≥ 45 mg L^{-1}. Thus, taking into account the sensitivity and the accuracy of the method, [Cu(II)] = 25 mg L^{-1} in the supporting electrolyte seemed to be the optimal value. In addition, the increase of the Cu(II) concentration in the supporting electrolyte was accompanied by a shift of the peak potentials from ∼−750 mV to ∼−800 mV due to the formation of intermetallic compounds with different Cu : As ratio [27].

3.1.2 *Validation of the optimised voltammetric parameters*

3.1.2.1 *Deposition potential E_{dep}.* After the optimisation of the HCl and Cu(II) concentrations in the supporting electrolyte, the effect of these modifications on the initial voltammetric parameters was evaluated. In this way, in 2 M HCl and 25 mg L^{-1} Cu(II), the deposition potential was varied from −0.35 V to −0.55 V according to literature [11,12,26,29,30]. Deposition potentials $E_{dep} < -0.55$ V were not tested because, according to Profumo *et al.* [30], in HBr = 0.45 M and Cu(II) = 50 mg L^{-1}, the background line worsens and a second peak appears probably due to the formation of a different intermetallic compound [26]. Furthermore, values of $E_{dep} > -0.35$ V were also not tested because (i) peak current dropped almost completely for $E_{dep} > -0.375$ V in HCl = 2 M at a hanging copper amalgam drop working electrode [28] and (ii) for $E_{dep} > -0.30$ V, the incomplete reduction of As(III) to As(0) leads to an absence of the As(III) peak [26].

For $-0.41 > E_{dep} \geq -0.49$ V and $-0.41 < E_{dep} \leq -0.35$ V, a decrease of the peak intensity of more than 60% was observed (Figure 2). Thus, in this study, the determination of As(III) was done at $E_{dep} = -0.41$ V in order to improve the sensitivity of the method and the ratio 'Peak intensity/Background current' confirmed this choice. This potential is in accordance with the value optimised by Li and Smart [26] and Profumo *et al.* [30] with Cu(II) = 50 mg L^{-1}, $T_{dep} = 60$ s and during SWCSV – HMDE and DPCSV – HMDE methods, respectively.

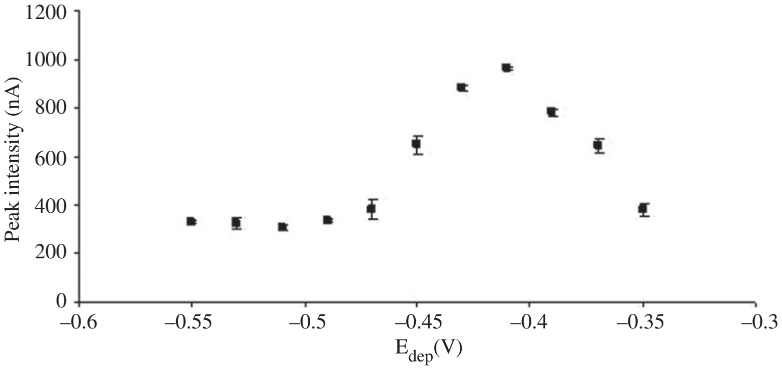

Figure 2. Evolution of As(III) peak intensity as a function of deposition potential (supporting electrolyte: 2 M HCl, 25 mg L^{-1} Cu(II), T_{dep} 50 s and 5 µg As(III) L^{-1}) – Error bars for $n = 3$.

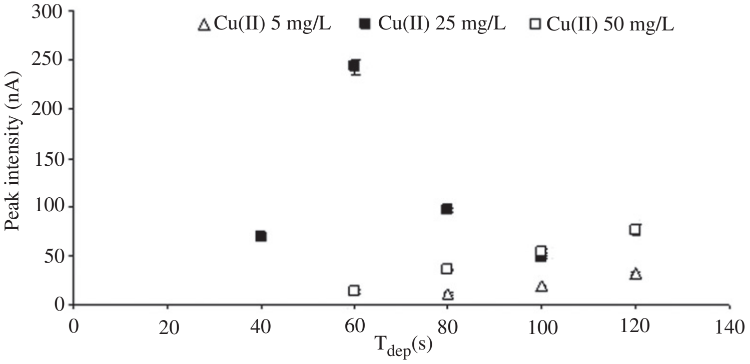

Figure 3. Evolution of As(III) peak intensity as a function of deposition time and Cu(II) concentration (supporting electrolyte: 2 M HCl, E_{dep} –0.41 V and 1 µg As(III) L^{-1}) – Error bars for $n = 3$.

3.1.2.2 *Deposition time T_{dep}*. The deposition time has always been considered as an important factor in CSV analysis because of its prevailing influence on sensitivity of the method [28]. Several authors previously demonstrated that the peak current increases with the deposition time until a maximum is reached. The decrease in the peak current for longer deposition time is probably due to a change in the stoichiometry of the As–Cu compound formed because of the occurrence of a different concentration ratio at the electrode surface [26]. However, the optimisation of the deposition time also depends on the Cu(II) concentration added in the supporting electrolyte [11,12,26,28].

The optimisation of this deposition time (Figure 3) was thus done in 2 M HCl and for different Cu(II) concentrations (5, 25 and 50 mg L^{-1}). These concentrations were chosen according to the results obtained either in the present study or previously reported by several authors.

Highest peak intensities and lowest background currents were obtained for Cu(II) = 25 mg L^{-1} and $T_{dep} = 60$ s. A 5 mg L^{-1} Cu(II) concentration required a minimum deposition time of 80 s to quantify 1 µg As(III) L^{-1} and the peak intensity obtained is reduced by 90% and 70% when compared to those obtained with Cu(II) concentrations of 25 and 50 mg L^{-1}, respectively. Indeed, as already shown by others [11,26], longer deposition times are required to improve sensitivity for low Cu(II) concentrations. For 50 mg L^{-1} Cu(II), the peak intensity increased with the deposition time applied. Thus, a better sensitivity than with Cu(II) = 25 mg L^{-1} could have been obtained for deposition times longer than 120 s. However, in order to reconcile short deposition time, high sensitivity and good accuracy, a deposition time of 60 s and a Cu(II) concentration of 25 mg L^{-1} were chosen.

Table 2 presents the optimised voltammetric parameters used for the quantification of As(III) in this study after having tested their influence on the peak shape and height and on the residual background current.

These optimised voltammetric and chemical parameters allowed attempting quantification limit of 0.5 μg As(III) L^{-1}. The Relative Standard Deviation value of three replicates samples was below 5% for [As(III)] < 1 μg L^{-1}. Furthermore, very good determination coefficients were obtained for 9 replicates. The equations of the calibration curves were the following:

$$\surd\ \text{As(III) peak intensities} = (-2.29 \pm 0.02)[\text{As(III)}] + (1.11 \pm 0.15)$$
$$\text{for } 1.0 \leq [\text{As(III)}] \leq 10\ \mu\text{g L}^{-1} \text{ with } r^2 = 0.9992,$$
$$\surd\ \text{As(III) peak intensities} = (-1.88 \pm 0.02)[\text{As(III)}] + (0.72 \pm 0.02)$$
$$\text{for } 0.5 \leq [\text{As(III)}] \leq 1.0\ \mu\text{g L}^{-1} \text{ with } r^2 = 0.9995.$$

Moreover, regarding the slopes of the calibration curves, it is required to differentiate the two concentration ranges and to use two different calibration curves for the quantification depending on As(III) concentration. The use of the more restricting standard addition method could resolve this problem.

3.2 *Validation of the method with ultrapure and reconstituted water*

3.2.1 *Validation of the optimised SW-CSV method*

In order to validate the method and to take into account the interferences of ionic species present in the sample matrix, several As(III) concentrations were determined in both ultrapure grade water and model water (Table 1). Figure 4 presents the polarograms obtained for the quantification of 2.1 μg As(III) L^{-1} in model water. The objective of this experiment was to evaluate the adaptability of the method on a complex matrix and its performance taking into account accuracy.

First, possible effects from interfering species would be identified by comparing the equation of calibration curves in model and ultrapure grade waters. In model water, very good determination coefficients were also obtained for 9 replicates and the equations of the calibration curves were:

$$\surd\ \text{As(III) peak intensities} = (-2.31 \pm 0.02)\ [\text{As(III)}] + (0.97 \pm 0.14)$$
$$\text{for } 1.0 \leq \text{As(III) concentrations} \leq 10\ \mu\text{g L}^{-1} \text{ with } r^2 = 0.9994,$$
$$\surd\ \text{As(III) peak intensities} = (-2.00 \pm 0.02)[\text{As(III)}] + (0.06 \pm 0.02)$$
$$\text{for } 0.5 \leq \text{As(III) concentrations} \leq 1\ \mu\text{g L}^{-1} \text{ with } r^2 = 0.9992.$$

Thus, the differentiation of the two concentration ranges and the use of two different calibration curves were also required for the quantification. Besides, the comparison of the

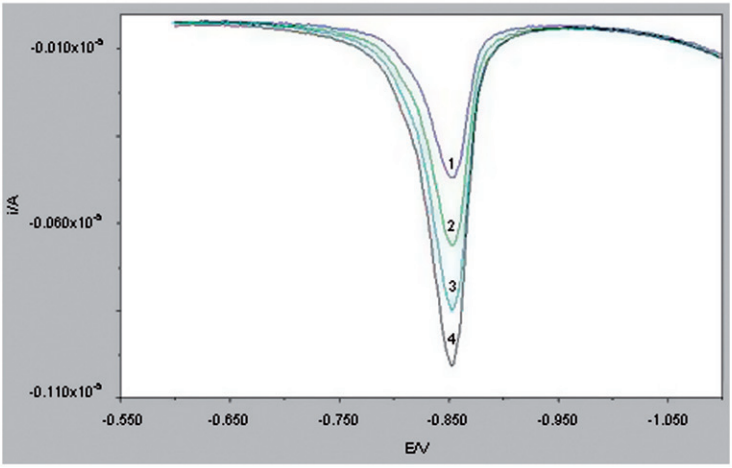

Figure 4. Polarograms obtained for the quantification of 2.1 µg As(III) L^{-1} in model water by SW-CSV and with standard addition method ([HCl] = 2 M, [Cu(II)] = 25 mg L^{-1}, $E_{dep} = -0.41$ V, $T_{dep} = 60$ s). 1 – As(III) sample, 2 – Standard addition 1 (As(III) = 1 µg L^{-1}), 3 – Standard addition 2 (As(III) = 1.5 µg L^{-1}), 4 – Standard addition 3 (As(III) = 2 µg L^{-1}).

slopes of calibration curves obtained in ultrapure grade and model waters underlined that a low mineral content had no influence on this optimised SW-CSV method.

Secondly, several model water and ultrapure grade water samples were spiked with $0.7 \leq$ As(III) concentrations ≤ 9.80 µg L^{-1}. The results of the quantifications by the standard addition method are given in Table 3 with the parameters of standard additions curves and the determination coefficients. These quantifications were done in 2 M HCl and 25 mg L^{-1} Cu(II) with the optimised voltammetric parameters reported in Table 2. An evaluation of errors on analytical measurements and experimental procedure was made possible by triplicating both measures and experiments.

Table 3 reports good determination coefficients by SW-CSV both in ultrapure grade water and model water. In addition, the standard deviation on slopes obtained for 9 replicates were low (≤ 0.11 for $-2.35 \leq$ standard addition curve slopes ≤ -1.45) highlighting a good repeatability. For As(III) = 0.7 µg L^{-1}, as expected, recovery percentages were less precise (119 ± 10% in ultrapure grade water and 109 ± 2% in model water) because of the quantification limit of the method. However, for As(III) $\geq$ 1.4 µg L^{-1}, good recovery percentages (101 ± 4%) were obtained both in ultrapure grade water and model water. Thus, this optimised voltammetric method appeared to be suitable for arsenic analysis in model water samples presenting low mineral content because it is easy to handle, rapid and repeatable (uncertainties on the measurements ≤ 0.1 and 0.4 for As(III) concentrations ≤ 2.1 µg L^{-1} and between 4.9 and 9.8 µg L^{-1}, respectively). Good recoveries of As(III) spiked samples were obtained without any electrodes or sample preparation steps and the quantification of [As(III)] = 0.5 µg L^{-1} has been verified to be accurate and repeatable (in the present study only [As(III)] $\geq$ 0.7 µg L^{-1} were determined).

3.2.2 *Comparison with the HG-AAS method*

The optimised voltammetric method was then compared with the HG-AAS method. In this way, this spectrometric method (with standard additions procedure) was applied

Table 3. Determination of As(III) by SW-CSV in ultrapure and model water by standard additions method ($n=9$, peak intensity and As(III) concentrations are respectively expressed in μA and μg L^{-1}) – Values of the standard additions of As(III) made in each case.

		Ultrapure grade water			Model water		
As(III) initial concentration (μg L^{-1})	As(III) standard additions (μg L^{-1})	Standard addition curve parameters	Determination coefficient r^2	Recovered concentration (μg L^{-1})	Standard addition curve parameters	Determination coefficient r^2	Recovered concentration (μg L^{-1})
0.70	0.50, 0.60, 0.70	$a=-1.74\pm0.03$ $b=-1.47\pm0.04$	0.9992	0.84 ± 0.07	$a=-1.69\pm0.03$ $b=-1.40\pm0.04$	0.9989	0.76 ± 0.02
1.40	0.7, 1.0, 1.4	$a=-2.00\pm0.05$ $b=-3.0\pm0.1$	0.9981	1.5 ± 0.1	$a=-1.56\pm0.04$ $b=-2.33\pm0.09$	0.9981	1.42 ± 0.07
2.10	1.0, 1.5, 2.0	$a=-1.80\pm0.05$ $b=-4.2\pm0.1$	0.9977	2.30 ± 0.05	$a=-1.6\pm0.1$ $b=-0.8\pm0.3$	0.9959	2.04 ± 0.05
4.90	2.0, 3.0, 4.0	$a=-2.08\pm0.02$ $b=-10.1\pm0.1$	0.9998	4.9 ± 0.1	$a=-1.47\pm0.04$ $b=-7.9\pm0.2$	0.9977	5.0 ± 0.1
8.40	4.0, 6.0, 8.0	$a=-2.03\pm0.02$ $b=-17.4\pm0.2$	0.9999	8.4 ± 0.4	$a=-1.45\pm0.02$ $b=-12.6\pm0.2$	0.9993	8.3 ± 0.2
9.80	5.0, 7.0, 9.0	$a=-2.35\pm0.01$ $b=-23.8\pm0.2$	0.9999	9.8 ± 0.2	$a=-1.54\pm0.05$ $b=-16.4\pm0.6$	0.9970	9.7 ± 0.2

Note: Type of the standard addition curve equation: As(III) peak intensity = a[As(III)] + b with a: slope and b: ordinate.

Table 4. Determination of As(III) by HG-AAS in ultrapure and model water by standard additions method ($n = 9$; absorbance in arbitrary units, As(III) concentration in $\mu g\,L^{-1}$) – Values of the standard additions of As(III) made in each case.

		Ultrapure grade water			Model water		
As(III) initial concentration ($\mu g\,L^{-1}$)	As(III) standard additions ($\mu g\,L^{-1}$)	Standard addition curve parameters (a and b in $10^{\wedge -3}$)	Determination coefficient r^2	Recovered concentration ($\mu g\,L^{-1}$)	Standard addition curve parameters	Determination coefficient r^2	Recovered concentration ($\mu g\,L^{-1}$)
0.70	0.50, 0.60, 0.70	a = 6.1 ± 0.5 b = 4.0 ± 0.5	0.9943	0.7 ± 0.2	a = 6.2 ± 0.1 b = 5.4 ± 0.1	0.9999	0.73 ± 0.07
1.40	0.7, 1.0, 1.4	a = 6.5 ± 0.3 b = 8.3 ± 0.4	0.9980	1.5 ± 0.4	a = 5.8 ± 0.3 b = 9.4 ± 0.6	0.9970	1.6 ± 0.4
2.10	1.0, 1.5, 2.0	a = 5.1 ± 0.1 b = 11.5 ± 0.1	0.9999	2.25 ± 0.06	a = 5.4 ± 0.3 b = 11.8 ± 0.6	0.9929	2.3 ± 0.2
4.90	2.0, 3.0, 4.0	a = 5.4 ± 0.1 b = 27 ± 4	0.9992	4.9 ± 0.2	a = 5.1 ± 0.0 b = 26.4 ± 0.1	0.9999	5.2 ± 0.1
8.40	4.0, 6.0, 8.0	a = 5.0 ± 0.1 b = 44.1 ± 0.5	0.9996	8.9 ± 0.2	a = 5.2 ± 0.1 b = 45 ± 1	0.9987	8.4 ± 0.5
9.80	5.0, 7.0, 9.0	a = 5.0 ± 0.1 b = 50.8 ± 0.6	0.9992	10.1 ± 0.3	a = 4.9 ± 0.1 b = 52 ± 1	0.9986	10.8 ± 0.4

Note: Type of the standard addition curve equation: As(III) absorbance = a[As(III)] + b with a: slope and b: ordinate.

to ultrapure and model water samples spiked with the same As(III) concentrations (Table 4). Recovery percentages ranged from 99 ± 3% to 108 ± 25% in ultrapure grade water and from 100 ± 5% to 113 ± 26% in model water. It was thus underlined from these results that this method is as much exact as the polarographic one. Besides, good determination coefficients were obtained both in ultrapure and model waters and the standard deviations on slopes obtained for 9 replicates were also low. However, the main difference between the two methods was the repeatability in the measurements. Indeed, the uncertainties on measurements were higher with the spectrometric method and more specially for As(III) concentrations $\leq 2\,\mu g\,L^{-1}$.

Finally, the comparison of the slopes of standard addition curves obtained in ultrapure grade and model waters underlined that a low mineral content did not interfere with the analysis (difference in the slopes $\leq 10\%$).

It appeared from these results that the voltammetric SW-CSV method is more repeatable than the spectrometric HG-AAS one particularly for low As(III) levels. Thus, low As(III) concentrations ($\leq 2\,\mu g\,L^{-1}$) were quantified by SW-CSV and then the more rapid HG-AAS method was used for determination of higher As(III) amounts.

3.3 *Study of interferences on the spectrometric and voltammetric determinations*

In natural water samples, Fe(II) and Fe(III) can be present according to reductive or oxidising conditions and thus interfere on analytical results. Furthermore, for drinking water production, the coagulation/flocculation process, using Fe^{3+} or Al^{3+} ions, underlines good removal efficiencies for arsenic [19,21,22]. Iron is more efficient than aluminium and then more used. As a consequence, soluble Fe(III) can be found after treatment in samples matrix and interfere on the voltammetric or spectrometric determination of arsenic. A particular attention is also paid to the behaviour of As(V) against As(III) because As(III) oxidation could occur in samples matrix conditions. Moreover, it is known that groundwaters can contain low amounts of Natural Organic Matter (NOM). It was thus checked that until 2 mg Dissolved Organic Carbon L^{-1}, NOM effects on SW-CSV and HG-AAS signals did not prevent As(III) quantification. The interferences that could take place during the experimental procedure were the following: deposition on the HMDE, competition with As(III) in its reaction with copper, and formation of other intermetallic compounds [12].

3.3.1 *Evaluation of the iron species interferences*

An evaluation of the interferences of Fe(III) and Fe(II) on the SW-CSV and HG-AAS determinations was thus investigated for $100 \leq [Fe_{Tot}] \leq 1000\,\mu g\,L^{-1}$ (by $100\,\mu g\,L^{-1}$ steps) and for $[As(III)] = 5\,\mu g\,L^{-1}$, $10\,\mu g\,L^{-1}$ and $50\,\mu g\,L^{-1}$. Such concentrations were chosen because a European Directive [32] establishes a maximum iron content after drinking water production treatment of $200\,\mu g\ Fe_{Tot}\,L^{-1}$. The analytical methods were checked to be efficient in the presence of high Fe(III) and Fe(II) amounts if coagulation is not well performed and when natural water samples analysed are groundwater samples.

The interferences on both methods were low and independent of the Fe/As ratio varying from 2 to 200. Indeed, whatever the As(III) concentration was a value such as $100 \leq [Fe(III)] \leq 1000\,\mu g\,L^{-1}$ caused a 10% decrease of the As(III) signal during SW-CSV and HG-AAS whereas the same Fe(II) concentrations did not cause any decrease in the signal. Thus, the quantification of As(III) by these two methods cannot be done by a calibration curve but rather by standard additions which allows to get free from the necessity to use two different calibration curves for As(III) quantification by SW-CSV as seen previously.

The results related to SW-CSV method are in accordance with Ferreira and Barros [12] who underlined no interferences of Fe(II) species at concentrations in the order of magnitude of those found in groundwaters. Furthermore, Fe(III) species cause high interferences but only for concentrations above those expected in mineral waters. Moreover, Feeney and Kounaves [8], in the development of a voltammetric method at a gold ultramicroelectrode, studied the interference of several metals and their results showed a 10% decrease in the As(III) current signal for $100 \leq [\mathrm{Fe_{Tot}}] \leq 500\,\mu\mathrm{g\,L^{-1}}$. Jiajie and Nagaosa [33], employing an edge-plane pyrolytic graphite disk as working electrode, tolerated $[\mathrm{Fe_{Tot}}] \leq 800\,\mu\mathrm{g\,L^{-1}}$ for the quantification of 1 μg As(III) $\mathrm{L^{-1}}$. However, other results are in contradiction with those previously described. He *et al.* [27] and Profumo *et al.* [30] pointed out no interferences of iron species until $20\,\mathrm{mg\,L^{-1}}$ and $10\,\mathrm{mg\,L^{-1}}$, respectively. Moreover, Piech and Kubiak [31], by using CSV under specific experimental conditions, underlined no Fe(II) and Fe(III) interferences for Fe/As ratios up to 1000.

Results related to HG-AAS method and published in literature are rather scattered thus allowing only a few comparisons to ours. Anthemidis *et al.* [34], by using other chemical parameters, underlined no interference of Fe(II) and Fe(III) on the determination of 2 μg As(III) $\mathrm{L^{-1}}$ until a concentration of $10\,\mathrm{mg\,L^{-1}}$. The results of Bortoleto and Cadore [14], with HCl concentration 3 times lesser, showed a 30% decrease in the As(III) absorbance for $[\mathrm{Fe_{Tot}}] = 300\,\mu\mathrm{g\,L^{-1}}$. Michon [23] tolerated Fe(II) and Fe(III) concentrations lower than 250 times the As(III) concentration. Welz and Schubert-Jacobs [35] pointed out that an increase in HCl concentration improved the range of interference-free determination.

The influence of various mixtures of Fe(II) and Fe(III) was also investigated for $[\mathrm{As(III)}] = 10\,\mu\mathrm{g\,L^{-1}}$ and $[\mathrm{Fe_{Tot}}] = 200\,\mu\mathrm{g\,L^{-1}}$. The results did not highlight any particular tendency and the presence of $200\,\mu\mathrm{g\,L^{-1}}$ mixture of Fe(II) and Fe(III) caused a 3.3 ± 1.4% decrease of the As(III) SW-CSV signal and a 11.1 ± 4.4% decrease of the As(III) HG-AAS signal which is in agreement with the results mentioned above.

3.3.2 *Interferences by As(V) species*

As As(III) can coexist with As(V) in natural water samples, it has been verified that As(V) do not interfere with As(III) quantifications. As a consequence, the evolution of the As(III) signal in the presence of increasing concentrations of As(V) from 5 to $50\,\mu\mathrm{g\,L^{-1}}$ was tested for SW-CSV and HG-AAS methods. No interference on either method was caused by the presence of As(V) in the sample. Indeed, the As(III) signal reduction percentage was lower than 10%, whatever the As(III) and As(V) concentrations. These results could be expected because the electrochemically inactive As(V) species cannot be detected directly by an electrochemical technique such as voltammetry and because in the HG-AAS method, all chemical parameters were optimised in order to allow the specific As(III) analysis.

4. Conclusion

Laboratory voltammetric and spectrometric methods were optimised for As(III) quantification in model water with low mineral content and in the presence of interfering species.

Main conclusions were the following: (i) voltammetry is more sensitive and repeatable than spectrometry to determine low As(III) concentrations in high iron levels samples and (ii) the standard addition method is required for an accurate quantification in order to determine As(III) concentrations between 0.5 and 10 $\mu g\,L^{-1}$ without changing experimental conditions and to avoid iron and NOM interferences. The voltammetric method, whose quantification limit is 0.5 $\mu g\,L^{-1}$, was thus chosen to analyse low As(III) concentrations ($[As(III)] \leq 2\,\mu g\,L^{-1}$).

Acknowledgements

The authors thank the 'Regional Council of Limousin' for the grants assigned to the development of this project; VP thanks the French Ministry of Universities for the Ph.D. allocation received.

References

[1] B.K. Mandal and K.T. Suzuki, Talanta **58**, 201 (2002).
[2] K. Bell, J. Cohen, S. Foster, E. Hack, R. Iwamiya, D. Kaczka, J. Koplos, F. Latkiewicz, A. Schulman, B. Smith, and J. Wu, US-EPA Report No. EPA-815-R-00-023, 2000.
[3] P.L. Smedley and D.G. Kinniburgh, Appl. Geochem. **17**, 517 (2002).
[4] A.H. Smith, E.O. Lingas, and M. Rahman, Bull. World Health Org. **78**, 1093 (2000).
[5] M.F. Hughes, Toxicol. Lett. **133**, 1 (2002).
[6] D.Q. Hung, O. Nekrassova, and R.G. Compton, Talanta **64**, 269 (2004).
[7] Y.C. Sun, J. Mierzwa, and M.H. Yang, Talanta **44**, 1379 (1997).
[8] R. Feeney and S.P. Kounaves, Talanta **58**, 23 (2002).
[9] S.B. Rasul, A.K.M. Munir, Z.A. Hossain, A.H. Khan, M. Alauddin, and A. Hussam, Talanta **58**, 33 (2002).
[10] Y. Song and G.M. Swain, Anal. Chim. Acta **593**, 7 (2007).
[11] C.M. Barra and M.M. Correia dos Santos, Electroanalysis **13**, 1098 (2000).
[12] M.A. Ferreira and A.A. Barros, Anal. Chim. Acta **459**, 151 (2002).
[13] W. Holak, Anal. Chem. **52**, 2189 (1980).
[14] G.G. Bortoleto and S. Cadore, Talanta **67**, 169 (2005).
[15] S. Maity, S. Chakravarty, P. Thakur, K.K. Gupta, S. Bhattacharjee, and B.C. Roy, Chemosphere **54**, 1199 (2004).
[16] C. Roussel, H. Bril, and A. Fernandez, J. Environ. Qual. **29**, 182 (2000).
[17] R.C. Cheng, S. Liang, H.C. Wang, and M.D. Beuhler, J. Am. Water Works Assoc. **86**, 79 (1994).
[18] J. Gregor, Water Res. **35**, 1659 (2001).
[19] D.L. Boccelli, M.J. Small, and D.A. Dzombak, Environ. Sci. Technol. **39**, 6501 (2005).
[20] S. Song, A. Lopez-Valdivieso, D.J. Hernandez-Campos, C. Peng, M.G. Monroy-Fernandez, and I. Razo-Soto, Water Res. **40**, 364 (2006).
[21] M. Edwards, J. Am. Water Works Assoc. **86**, 64 (1994).
[22] E.O. Kartinen and C.J. Martin, Desalination **103**, 79 (1995).
[23] J. Michon, Ph.D. thesis, University of Limoges, 2006.
[24] V. Lenoble, C. Chabroullet, R. Al Shukry, B. Serpaud, V. Deluchat, and J.C. Bollinger, J. Colloid Interface Sci. **280**, 62 (2004).
[25] U. Greulach and G. Henze, Anal. Chim. Acta **306**, 217 (1995).
[26] H. Li and R.B. Smart, Anal. Chim. Acta **325**, 25 (1996).
[27] Y. He, Y. Zheng, M. Ramnaraine, and D.C. Locke, Anal. Chim. Acta **511**, 55 (2004).
[28] R. Piech, B. Baś, E. Niewiara, and W.W. Kubiak, Talanta **72**, 762 (2007).

[29] M.S. Pereira, E. Winter, J.R. Guimarães, S. Rath, and A.H. Fostier, Environ. Chem. Lett. **5**, 137 (2007).
[30] A. Profumo, D. Merli, and M. Pesavento, Anal. Chim. Acta **539**, 245 (2005).
[31] R. Piech and W.W. Kubiak, J. Electroanal. Chem. **599**, 59 (2007).
[32] EU Council Directive 98/83/EC of 3 November 1998 relative to the quality of drinking water. Off. J. Europ. Union L330, 32 (1998).
[33] L. Jiajie and Y. Nagaosa, Anal. Chim. Acta **593**, 1 (2007).
[34] A.N. Anthemidis, G.A. Zachariadis, and J.A. Stratis, Anal. Chim. Acta **547**, 237 (2005).
[35] B. Welz and M. Schubert-Jacobs, J. Anal. At. Spectrom. **1**, 23 (1986).