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Sequential Injection Anodic Stripping Voltammetry at Tubular Gold Electrodes for Inorganic Arsenic Speciation

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1. Introduction

Arsenic is one of the most feared contaminants because of its high toxicity at low concentrations. Exposure to high levels of arsenic can cause problems in humans ranging from gastrointestinal symptoms to arsenicosis. Once this element is dissolved in water and is ingested, it is accumulated in the body. Contamination of groundwater with arsenic is one of the major environmental and public health problems on a global scale (NRC, 1999).

The World Health Organization guideline has established a concentration of $10 \mu\text{g l}^{-1}$ as the maximum residue limit for arsenic in drinking water (WHO, 2004). Well-known arsenic contaminated regions include Bangladesh, India and other countries. In Mexico, sources of drinking water exceeding $10 \mu\text{g l}^{-1}$ have been found in Baja California Sur, Chihuahua, Coahuila, Durango, Zacatecas, Hidalgo, Morelos, Guanajuato, Sonora and San Luis Potosí (Camacho et al., 2011). In Spain, the presence of naturally occurring arsenic in groundwater has been reported in the sedimentary Duero and Tajo Cenozoic basins, located in central Spain (García-Sánchez et al., 2005; Gómez et al., 2006; Vega et al., 2008).

Arsenic is usually distributed as water soluble species, colloids, suspended forms and sedimentary phases. Mobilized arsenic is most likely transported by water and accumulated in downstream river sediments as a result of the great affinity of arsenic to iron rich phases. The most common sources of non-naturally arsenic worldwide arise from the presence of alloys used in manufacture of transistors, laser, semi-conductors and mining industry (Smedley & Kinniburgh, 2002).

There are more than 20 arsenic compounds identified in environmental and biological systems (Gong et al., 2002). The dominant forms of arsenic present in the environment are As(III) (arsenite) and As(V) (arsenate) (Mondal, 2006). As(III) binds to sulfhydryl groups impairing the function of many proteins and affects respiration by binding to the vicinal thiols in pyruvate dehydrogenase and 2-oxoglutarate dehydrogenase. As(V) is a molecular

analogue of phosphate and inhibits oxidative phosphorylation, the main energy generation system. As(V) is most frequently present in surface water while As(III) is commonly found in anaerobic groundwaters. Redox potential, pH and organic matter control the species present in water.

To determine the potential transformation and risk of arsenic in the environment, the analysis of arsenic should include identifying and quantifying both, the total quantity of arsenic present and the specific chemical forms, a procedure known as speciation (Bednar et al., 2004; Burguera & Burguera, 1997; Gong et al., 2002).

2. Arsenic speciation

In-house laboratory assays are generally required to accurately measure arsenic in environmental samples at the $\mu\text{g l}^{-1}$ level in waters. The preferred laboratory methods for measurement of arsenic involve sample pre-treatment, either with acid addition or acidic digestion of the sample. Pre-treatment transfers all the arsenic in the sample into an arsenic acid solution, which is subsequently measured using techniques such as graphite furnace atomic absorption spectroscopy (ETAAS), atomic fluorescence spectrometry (AFS), inductively coupled plasma atomic emission spectrometry (ICP-AES), inductively coupled plasma-mass spectrometry (ICP-MS), high performance liquid chromatography (HPLC) coupled to ICP-MS, X-ray fluorescence (XRF), neutron activation analysis (NAA) and capillary electrophoresis (CE) (B'Hymer & Caruso, 2004; Burguera & Burguera, 1997; EPA, 1999; Gong et al., 2002; Melamed, 2005).

The most commonly used speciation techniques often involve a combination of chromatographic separation with spectroscopic detection. HPLC is the most used in the ion-pairing and ion exchange modes (B'Hymer & Caruso, 2004; Gong et al., 2002). Such techniques are expensive to operate and maintain and require fully equipped and staffed laboratories.

Anion- and cation-pairing chromatography techniques have been developed for separation of arsenic species. Tetrabutylammonium is the common pairing cation for separating As(III) and As(V) using reverse phase columns for the separation. The resolution depends on the concentration of ion-pair reagent, the flow rate, ionic strength and pH of the mobile phase (Guerin et al., 1999). Anion-exchange chromatographic techniques have been used for inorganic arsenic speciation analysis. A gradient elution using ammonium phosphate as mobile phase allows the resolution of As(III) and As(V) from organoarsenic species (Terlecka, 2005). Speciation of trace levels of arsenic in environmental samples requires high sensitivity, then the use of HPLC-MS with electrospray ionization, or HPLC-ICP-MS are often needed (B'Hymer & Caruso, 2004).

On the other hand, electrochemical assays, in particular stripping analysis, have demonstrated to be useful for detection of arsenic traces in water samples. Cathodic stripping voltammetry (CSV) or adsorptive cathodic stripping voltammetry (AdCSV) using hanging mercury drop electrodes (HMDE) was used in the past for arsenic analysis (Ferreira & Barros, 2002; Sadana, 1983). In the last years the analytical use of mercury has been discouraged due to its toxicity. Different materials have been reported for the determination of arsenic, including platinum (Williams & Johnson, 1992), gold (Forsberg et al, 1975), bismuth (Long & Nagaosa, 2008), carbon substrates (Sun et al., 1997) and boron doped diamond (Ivandini, et al. 2006).

Anodic stripping voltammetry (ASV) provides an alternative technique for measuring inorganic arsenic in water samples. ASV at gold film electrodes (Sun et al. 1997) or solid gold electrodes (Kopanica & Novotny, 1998) have been extensively used for inorganic arsenic speciation as they allow to determine separately As(III) and total As. The analysis by ASV involves three major steps (Figure 1). First, the electrode surface is conditioned for analysis (cleaning the surface of the solid electrode and/or plating a gold film). The As(III) is then deposited as elemental arsenic on the working gold electrode by electrochemical reduction. After the deposition step, the elemental arsenic is electrochemically oxidized (stripped) back to As(III). As(V), the most stable form of the element in oxidizing environments, is determined after chemical or electrochemical (Muñoz & Palmero, 2005) reduction to As(III), total As is then determined and As(V) is calculated by difference between total As and As(III). The Environmental Protection Agency (EPA) has approved an analytical method (EPA, 1999) for arsenic determination in water samples based on the use of ASV at gold film electrodes.

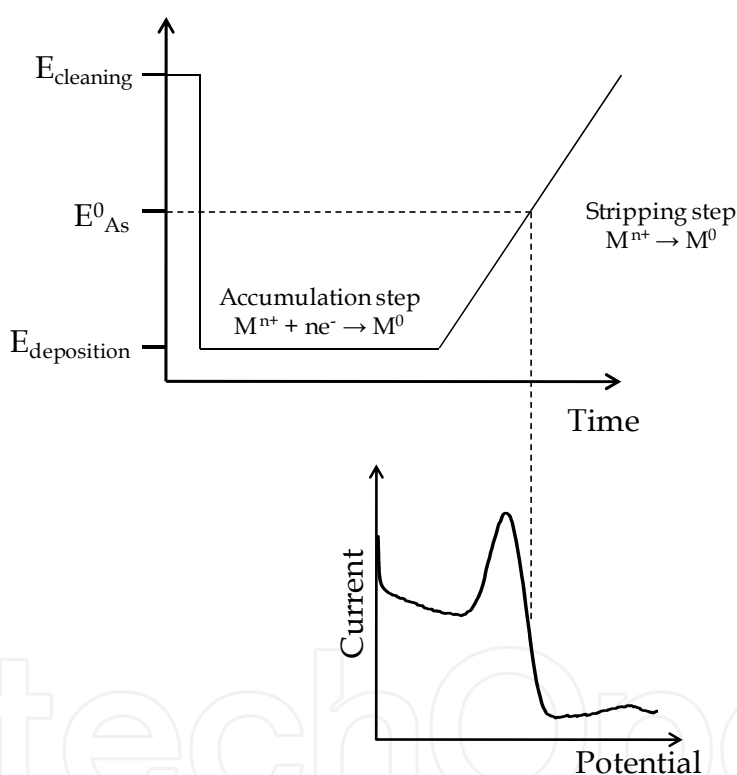


Fig. 1. Anodic stripping voltammetry: the potential-time waveform with the resulting voltammogram.

The remarkable sensitivity, broad scope and low cost of stripping analysis have led to its application in the determination of arsenic in water, soils and food samples. From early years of stripping analysis two main different research areas have been considered. The use of microelectrodes and disposable electrodes (Gibbon et al., 2010), and the development of hyphenated techniques using flow manifolds (Economou, 2010). On-line stripping analysis using flow analysis has demonstrated the viability and potentialities of this coupling such as: a) lower consumption of sample and reagents, b) higher precision and accuracy and c) higher degree of automation.

3. On-line stripping analysis

Flow analysis methodologies are based on the measuring of a transient non-steady signal, allowing a high sampling rate without the need for segmentation to limit analyte dispersion. This concept has simplified the measuring systems, and has resulted in a rapid increase in the interest of these techniques (Ruzicka & Hansen, 1988).

Continuous flow methodologies are the common approach for analysis by flow systems coupled to stripping analysis. This coupling mode uses a selection valve (SV), different streams of solutions are selected by the valve and pumped unidirectionally through the electrochemical flow cell for electrode modification/conditioning, pre-concentration and stripping (Fig.2). On-line medium exchange is an alternative to minimize the interference of the analytical matrix. The continuous flow mode is based on simple instrumentation, but its greatest drawback is the high consumption of sample and reagent solutions (Muñoz & Palmero, 2004).

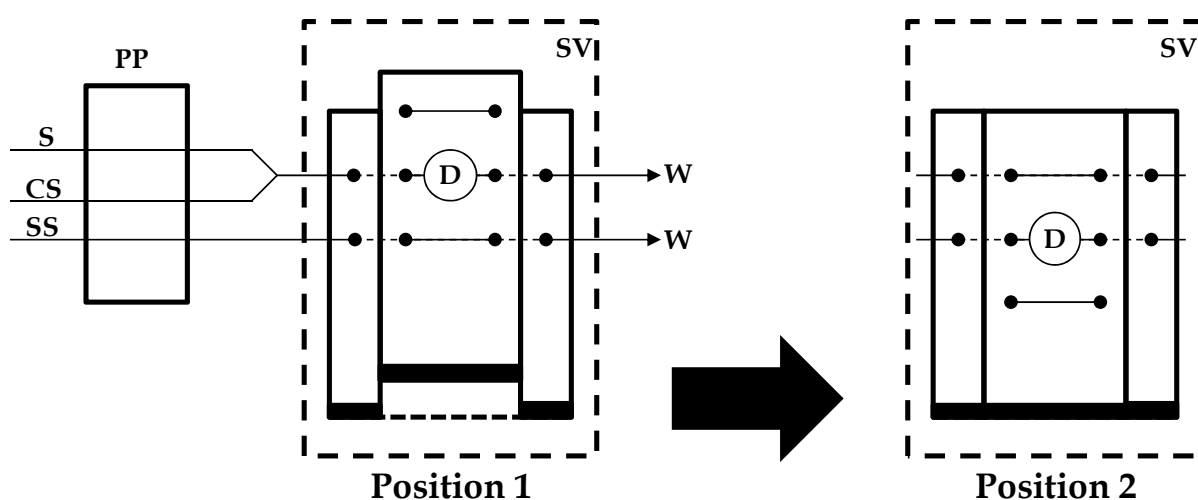


Fig. 2. Continuous flow system. S, sample; CS, conditioning solution; SS, stripping solution; PP, peristaltic pump; SV, selection valve; D, electrochemical flow cell; W, waste.

Flow injection analysis (FIA) is based on the injection of a known amount of sample in a flowing carrier solution stream via an injection valve (IV); the flowing carrier transports the sample to the detector. The main advantages of FIA compared with continuous flow systems are the operational simplicity and the lower consumption of sample and carrier (Bryce et al., 1995). However, the reduction in the amount of analyte deposited on the electrode surface as a result of the decrease in the contact time between the sample and the working electrode and the dispersion of the sample in the flow manifold results in a decrease of the analytical signal. A typical FIA system is illustrated in Fig. 3.

Sequential injection analysis (SIA, Fig. 4.) is other flow methodology that has been coupled to on-line stripping analysis. The heart of SIA manifold is the multiport selection valve; solutions are aspirated and transported as zones using a bidirectional pump. SIA advantages are the low consumption of sample and reagents, the flexibility and the potential for automated sample manipulation (Ivaska & Kubiak, 1997). The sample volumes used in SIA are smaller than those employed for continuous flow systems and FIA, the amount of analyte deposited is lower, thus yielding a decreased signal.

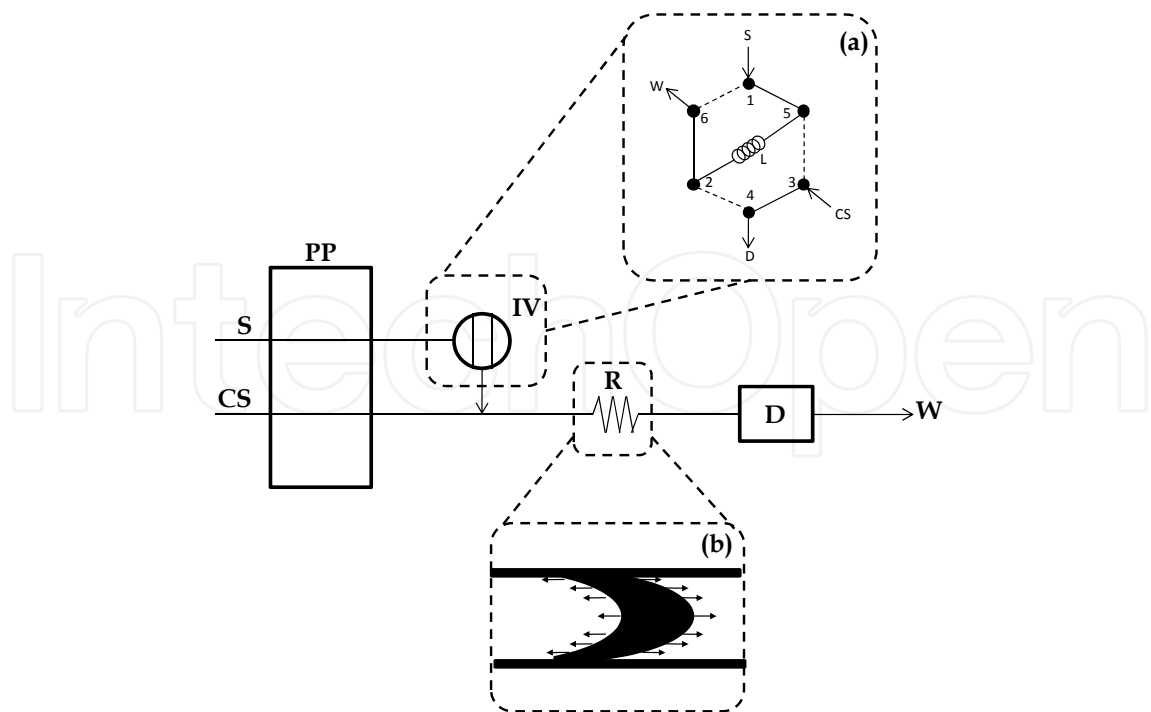


Fig. 3. Flow injection analysis system. a) insertion of S into CS, b) dispersion phenomena. S, sample; CS, carrier solution; PP, peristaltic pump; IV, injection valve; R, reactor; D, electrochemical flow cell; W, waste.

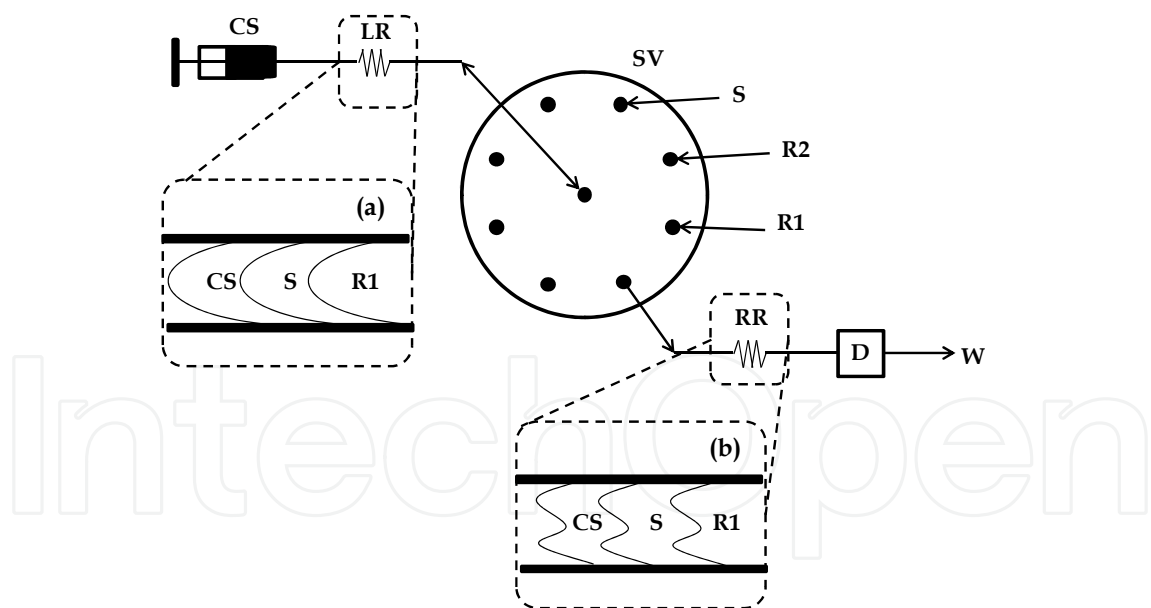


Fig. 4. Sequential injection analysis system. a) sample and reagents aspiration, b) mixture dispense. CS, carrier solution; LR, loading reactor; SV, selection valve; S, sample; R1 and R2, reagents; RR, reaction coil; D, electrochemical flow cell; W, waste.

Another critical part of flow methods is the detector (electrochemical flow cell). An electrochemical detector uses the electrochemical properties of analytes for determination in the flowing stream. Electrochemical detection is usually performed by controlling the potential of the working electrode at a fixed value and monitoring the current as a function

of time. The current response thus generated is proportional to the concentration of the analyte. During on-line stripping analysis the analyte is pre-concentrated on the surface electrode in flowing conditions, whilst the stripping step can be done in flowing conditions or stopped flow (Economou, 2010).

Different cell designs have been used for electrochemical detection. The cell design must fulfil the requirements of high signal-to-noise ratio, low dead volume, well defined hydrodynamics, small ohmic drop, high contact area and easy of construction and maintenance. In addition, the reference and counter electrodes should be located downstream next to the working electrode, so that reaction products at counter electrode or leakage from the reference electrode do not interfere with the working electrode detection.

The most widely used detectors are based on the wall-jet, thin-layer, and tubular configurations (Fig. 5.) (Trojanowicz, 2009):

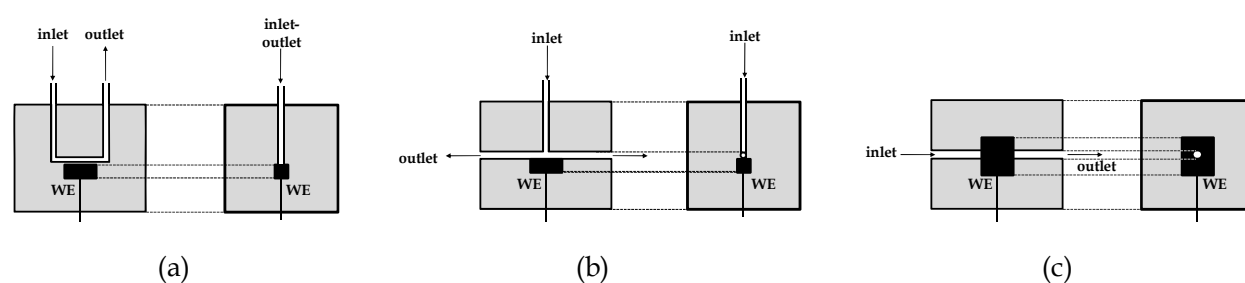


Fig. 5. Schematic representation of front and side view of electrochemical flow cells configurations. a) thin-layer, b) wall-jet and c) tubular. WE, working electrode.

In the wall-jet design, the stream flows perpendicularly to the working electrode surface, and then spreads radially over it improving the contact between the analyte and the electrode. The thin-layer cell consists on a thin layer of solution that flows parallel to the planar electrode surface, the main disadvantage is the small contact area. Tubular configuration provides minimal flow disturbance and a higher contact area, compared with thin-layer configuration. This feature has enabled the application of tubular configuration in flow injection systems with sequential determination in which the detector is relocated inside the flow manifold (Catarino et al., 2002).

4. Experimental conditions

4.1 Reagents, equipment and analysis

All solutions were prepared by dissolving the respective analytical grade reagent in ultrapure water (Milli Q, Millipore) with a specific conductivity lower than $0.1 \mu\text{S cm}^{-1}$, and used without further purification.

A stock solution of $1000 \text{ mg l}^{-1} \text{ As(V)}$ was prepared by dissolution of $\text{Na}_2\text{HAsO}_4 \cdot 7\text{H}_2\text{O}$ (Panreac, Spain) in water and acidified with concentrated HCl (0.1% v/v). A stock solution of $1000 \text{ mg l}^{-1} \text{ As(III)}$ was prepared by dissolving As_2O_3 (Sigma, St Louis, MO, USA) with NaOH $1 \times 10^{-2} \text{ M}$ (Panreac) and then acidified to pH 1 with concentrated HCl (Panreac). Stock solutions were renewed weekly. Standard solutions of As(V) and As(III) of concentrations ranging from 0 to $50 \mu\text{g l}^{-1}$ were prepared daily by dilution of the respective stock solution.

L-cysteine 1×10^{-3} M ($\text{HOOC-CH}(\text{NH}_2)\text{-CH}_2\text{-SH}$, Sigma) was used as reducing agent. A supporting electrolyte solution of 2.0 M HCl was used for all the experiments.

Figure 6 shows a scheme of the sequential injection anodic stripping voltammetry system (SI-ASV) used for inorganic arsenic speciation in water samples. The system consisted of a MicroBu 2030 multisyringe burette with programmable speed (CS, Crison, Spain) used to aspire and dispense the reagent solutions, an eight-way selection valve (SV, Crison), a home-made tubular electrochemical cell (D), and a mixer chamber (MC).

The tubular electrochemical detection cell was made up of a Perspex body in which working and auxiliary electrodes were placed. These electrodes were built from gold and carbon discs (7.0 mm diameter) with length of 1.0 and 2.0 mm, respectively. Both have a tubular channel (0.8 mm diameter) in the centre of the electrode. These electrodes were used in connection with a saturated Ag/AgCl reference electrode (Metrohm, Switzerland). The instrumental devices were controlled by means of the Autoanalysis 5.0 software (Sciware, Spain). All tubing connecting the different components of the flow system was made of Omnifit PTFE with 0.8 mm (i.d.). Electrochemical experiments were performed with an Autolab PGSTAT10 potentiostat/galvanostat (EcoChemie) equipped with GPES 4.6 software. Unless otherwise stated, a frequency (f) of 25 Hz, pulse amplitude (E_{sw}) of 50 mV, step height (ΔE_s) of 8 mV, and deposition potential (E_d) and time (t_d) of -0.4 V for 40 s were chosen as the square wave anodic stripping voltammetry (SWASV) parameters. A conditioning potential and time (2 s at 2.0 V) was added to increase the reproducibility (Kopanica & Novotny, 1998).

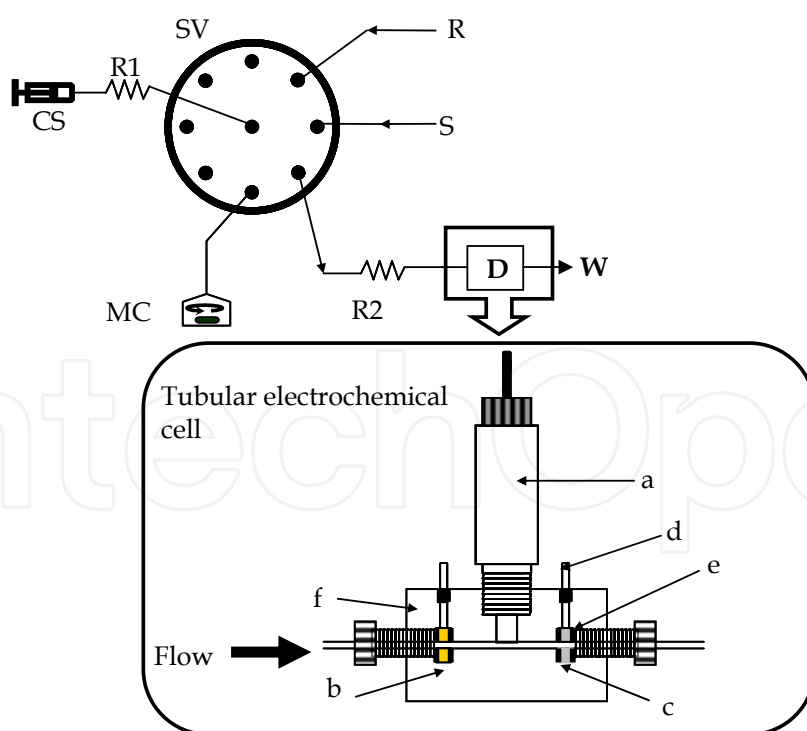


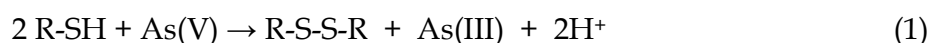
Fig. 6. Schematic set up of the SI-ASV flow system: CS, carrier solution; R1, holding coil; R2, reaction coil; SV, selection valve; R, reductant ; S, sample; MC, mixer chamber; D, detector; W, waste. Components of the electrochemical cell: a, reference electrode; b, tubular gold electrode; c, glassy carbon counter electrode; d, connector, e, O-ring.

4.1.1 Sampling

500 ml polyethylene bottles were conditioned by filling them with 2% v/v HNO₃ for at least three days. Once in the sampling site, bottles were rinsed several times with the water to be collected. Groundwater samples were obtained from deep and shallow wells in the area of Tierra de Pinares (Segovia, Spain), affected by arsenic contamination of aquifers. The well was pumped for at least 10 min before a water sample was collected. Bottles were completely filled with the sample to minimize the oxidation of As(III) by air. Immediately after sampling, the bottled water samples were acidified with HCl (pH<2), wrapped in hermetic plastic bags, and transported to the laboratory in iceboxes. Water samples were stored not longer than one week at 4°C prior analysis.

4.1.2 Analytical cycle

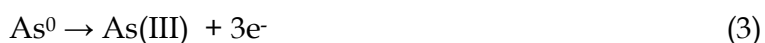
Initially, a 0.4 ml sample aliquot and a 0.2 ml of the reductant (L-cysteine, R-SH) are aspirated sequentially to the holding coil (R1). The resulting solution is directed towards the mixer chamber MC at 1.2 ml min⁻¹ (50 s), and is allowed to stand for 2 minutes to reduce chemically As(V) to As(III) according to the following reaction:



Simultaneous to the reduction of As(V) to determine in a second step total As, the measurement of As(III) was carried out. The sample was introduced in the system using a binary sampling strategy consisting on intercalation of multiple small sample segments of 50 µl (aspirated to S channel) with small segments (50 µl) of carrier solution (dispensed by CS to R2). The total aspirated volume was therefore 400 µl of sample and 250 µl of carrier solution. The binary sampling strategy creates multiple reaction interfaces which contribute to a faster homogenization of the sample media. The sample mixture is then propelled towards the electrochemical cell by the CS at a flow rate of 0.6 ml min⁻¹ to be electrochemically deposited (40 s at -0.4 V).



After deposition of elemental arsenic, 2.0 ml of the carrier solution are pumped through the detection cell at a flow rate of 30.0 ml min⁻¹. The elemental arsenic is then stripped off in stop flow mode using the CS as clean medium under the SWASV parameters mentioned above. The exchange of the sample solution by the CS electrolyte solution minimizes the interference produced by the chlorine generated at the auxiliary electrode (Billing et al., 2002).



For total As determination, the solution contained in the mixing chamber (port 4) is now aspirated to R1 and then propelled through the detection cell at a flow rate of 1.2 ml min⁻¹ (40 s). The resulting As(III) (sum of As(III) plus reduced As(V)) is then electrochemically reduced and stripped in a clean medium as described for As(III). The As(V) is then determined as the difference between total As and As(III).

5. Results and discussion

5.1 Optimization of the SI-ASV system for inorganic arsenic speciation

The optimization of the variables is a critical step in the design of new analytical methods. Optimization involves the selection of the chemical and instrumental factors which may affect the analytical signal, and the choice of the values of the variables to obtain the best response from the chemical system. For this purpose, two different strategies can be used. In the traditional univariate optimization, all values of the different factors except one are constant, and this one is the object of the examination. The alternative to this strategy is the use of chemometric techniques based mainly on the use of experimental designs (Tarley, et al. 2009).

Factorial designs are used to identify the significant variables (factors) affecting the selected response and as a tool to explore and model the responses as a function of these significant experimental factors. Two-level full factorial designs are a powerful alternative to find the adequate experimental conditions to produce the best response of the chemical system. This type of design fits the response to a linear model. For a two-factor case, the response surface is given by the linear model:

$$\hat{y} = b_0 + b_1x_1 + b_2x_2 + b_{12}x_1x_2 \quad (4)$$

If the interaction term $b_{12}x_1x_2$ is negligible, then the response surface is planar. The more important the interaction term, the greater is the degree of twisting that the planar response surface experiences. Chemometrical optimization commonly uses the following procedure: a) choose a statistical design to investigate the experimental region of interest, b) perform the experiments in random chronological order, c) perform analysis of variance (ANOVA) on the regression results so that the most appropriate model with no evidence of lack of fit can be used to represent the data.

The factors investigated that could affect the response for As(III) and total As determination are listed in Table 1. Two levels for each factor were selected for a complete factorial design (replicates, i.e., 2^{3+1}) allowing to identifying the critical factors. Sixteen experiments were performed in random order for each of As(III) and total As optimization. The optimal values obtained for factors B and C from the optimization of SI-ASV for As(III) were fixed for total As determination, and new factors related to the prior reduction of As(V) were included in the second design of experiments. The current of the stripping peak of arsenic (in μA) using a $10.0 \mu\text{g l}^{-1}$ standard of arsenic was selected as the response to be optimized.

The flow rate is critical in on-line stripping methods, as it controls the dispersion between the sample and the carrier solution. This factor and the deposition time contribute to the amount of analyte deposited on the electrode surface. With respect to the reaction coil length, it has to be sufficiently long for loading and pre-treatment of sample previous to the deposition step. In addition, for total As determination the chemical parameters such as reduction time and reducer concentration must guarantee the complete reduction of the As(V) contained in the sample to As(III).

Analyte	Variable	Level	
		-	+
As(III)	A. Flow rate (ml min ⁻¹)	0.6	1.2
	B. Deposition time (s)	20	40
	C. Reaction coil length (cm)	40.0	80.0
Total As	A. Flow rate (ml min ⁻¹)	0.6	1.2
	B. Reduction time (s)	120	300
	C. [L-cysteine] (M)	1×10 ⁻³	1×10 ⁻²

Table 1. Selected levels of each variable for the analysis of As(III) and total As.

The design matrix and mean values obtained for the peak height of the 10.0 µg l⁻¹ arsenic solution are provided in Table 2.

Exp	A	B	C	Mean peak height (µA) and %RSD	
				As(III)	Total As
1	-	-	-	2.14(5.29)	0.63(1.13)
2	-	-	+	13.35(1.59)	0.66(9.72)
3	-	+	-	5.58(7.35)	0.70(5.09)
4	+	-	-	7.26(2.53)	3.99(2.84)
5	-	+	+	12.20(1.16)	0.73(6.83)
6	+	+	-	4.41(3.05)	4.01(1.06)
7	+	-	+	9.53(2.67)	3.30(7.29)
8	+	+	+	8.89(1.03)	3.06(2.08)

Table 2. Design matrix and experimental results (mean and RSD, in brackets; n=2). A, B and C as in Table 1.

An Analysis of Variance of the results of the experimental design revealed the mean effect of each factor on the stripping signal (Table 3). In turn, these values enabled to calculate the variance of each factor using the Yates algorithm (column 3) (Massart, et al. 1997). By comparing the variance shown by each factor with the variance of the residuals, a Fischer F-test was then performed for each source of variation.

The F-test indicated that, at a significance level of p=0.05, the critical factors for As(III) determination were the deposition time, the length of the reactor R2 and the binary interactions flow rate-deposition time and flow rate-reaction coil length. The significance of the binary interactions is a consequence of the influence of both factors in the correct mixture of the sample solution and the electrolyte support solution. On the other hand, for total As determination, the variable with major contribution was the flow rate.

Figure 7 shows the effect of the control factors on the peak height of the stripping signal, among which the reaction coil length and the flow rate are the most important factors for As(III) and total As determination, respectively. Based on the results shown in Fig. 7, the combination of settings that generates the highest peak height was selected and is shown in Table 4.

Factor	As(III)			Total As		
	Effect	Variance	$F_{calculated}$	Effect	Variance	$F_{calculated}$
A	-0.80	2.54	6.86	2.91	33.96	403.08*
B	2.92	34.13	91.98*	-0.21	0.17	2.07
C	6.15	151.04	407.02*	-0.40	0.63	7.45
AB	-1.45	8.38	22.58*	-0.09	0.03	0.40
AC	-2.77	30.69	82.70*	-0.43	0.73	8.63*
BC	-0.60	1.42	3.82	-0.07	0.02	0.21
ABC	1.70	11.56	31.15*	-0.07	0.02	0.21
Residual		0.37			0.08	

Table 3. ANOVA of the results of the experimental design showing the factors and/or interactions affecting significantly the peak height ($F_{calculated}>7.57$ at 95% confidence level, in bold). A, B and C as in Table 1.

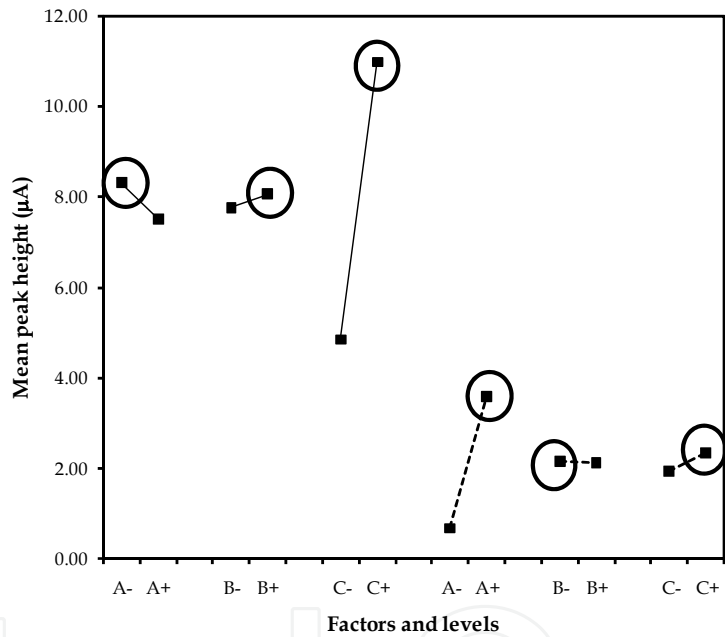


Fig. 7. Effect of control factors on the mean peak height of the stripping signal. (—) As(III) and (---) total As variables. A, B and C meaning as in Table 1. In circles the optimal level for each factor.

Analyte	Variable	Value
As(III)	A. Flow rate (ml min ⁻¹)	0.6
	B. Deposition time (s)	40
	C. Reaction coil length (cm)	80.0
Total As	A. Flow rate (ml min ⁻¹)	1.2
	B. Reduction time (s)	120
	C. [L-cysteine] (M)	1x10 ⁻²

Table 4. Optimized experimental conditions of SI-ASV system for inorganic arsenic speciation in water samples.

5.2 Analytical properties of the optimized flow system

Calibration plots for As(III) and total As (added as As(V)) were obtained in the experimental conditions described in Table 4. Three replicate measurements of each standard As solution were made and average values were used for calculations. A linear dependence of the height of the stripping signal with the injected concentration of arsenic was found in the concentration range 2-40 $\mu\text{g l}^{-1}$ for both total As and As(III) (Fig. 8.).

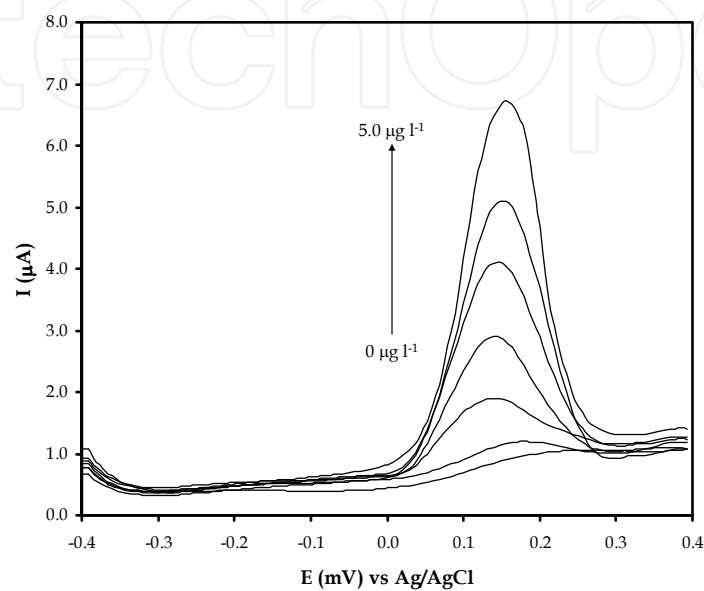


Fig. 8. SW-voltammograms for As(III) standards obtained by SI-ASV in 2M HCl.

The limit of detection calculated according to the IUPAC criterion as $3s_e/b_1$, where s_e is the square root of the residual variance of the calibration plot and b_1 is the slope, resulted in values of 1 $\mu\text{g l}^{-1}$ for As(III) and 2 $\mu\text{g l}^{-1}$ for total As. These limits of detection are adequate to assess the compliance of the method with the maximum tolerable levels for As in drinking water (WHO, 2004).

The reproducibility of the procedure, expressed as relative standard deviation of six replicate determinations of a water sample containing 5.0 and 30.0 $\mu\text{g l}^{-1}$ of As(III) and total As, were 3.6 and 7.6% respectively. The regression parameters of both regression lines are tabulated in Table 5.

Parameter	As(III)	Total As
Square root of residual variance, s_e	0.60	0.63
Determination coefficient, R^2	0.99	0.99
Intercept confidence interval, $b_0 \pm t s(b_0)$	0.43 ± 0.46	0.50 ± 0.52
Slope confidence interval, $b_1 \pm t s(b_1)$	1.27 ± 0.03	1.24 ± 0.04
Linear range ($\mu\text{g l}^{-1}$)	3-40	6-40
Limit of detection ($\mu\text{g l}^{-1}$)	1	2

Table 5. Regression parameters of the calibration plots of peak current (in μA) vs. arsenic concentration (in $\mu\text{g l}^{-1}$)

Technique	Electrode geometry	Working electrode	E_d (V), t_d (s)	LOD ($\mu\text{g l}^{-1}$)	Reference
Continuous flow	Wall-jet	Gold	-0.30, 300	0.15	Kopanica & Novotny, 1998
Continuous flow	Thin layer	Gold film	-0.2, 80	0.5	Huang & Dasgupta, 1999
Continuous flow	Wall jet	Gold film	-0.65, 60	100	Billing et al. 2002
Continuous flow	Wall jet	Gold film	-0.1, 120	0.55	Muñoz & Palmero, 2004
Continuous flow	Thin layer	Gold nanoparticles	-0.4, 600	0.25	Majid et al. 2006
SIA	Tubular	Gold	-0.4, 40	1.0	This work

Table 6. Compilation of on-line stripping techniques for As(III) determination.

Listed in Table 6 there are some methods designed for on-line ASV determination of As(III). Sample introduction by continuous flow is the main strategy used for on-line ASV. This tendency is related with the effort to increase sensitivity by increasing the amount of sample used. Tubular electrodes have higher contact area; this characteristic, in combination with the use of binary sampling strategy, generates a robust and sensitive flow system which is competitive with other flow systems proposed, but using less sample volume and shorter deposition time.

The developed flow system was applied to the determination of the inorganic species of arsenic in groundwater samples originating from Tierra de Pinares (Segovia, Spain) as described in the Experimental section. Five replicate determinations of both total As and As(III) were carried out on each sample by the standard additions method. Results are displayed in Table 7. Total As was also determined in samples by electrothermal atomic absorption spectrometry (ETAAS) for comparison.

Sample	SI-ASV system			ETAAS
	As(III)	As(V)	total As	total As
1	12	24	36	30
2	37	16	53	57
3	18	19	37	39
4	41	96	137	127
5	21	17	38	38
6	44	120	164	174
7	14	4	18	24
8	116	104	220	218
9	75	85	160	164
10	42	84	126	129

Table 7. Contents (mean, n=5) of As(III), As(V) and total As, determined in groundwater samples by the proposed SI-ASV system, and comparison between total arsenic concentrations determined by SI-ASV and ETAAS. Concentration units, $\mu\text{g l}^{-1}$.

For each groundwater sample, average total As concentrations determined by both methods were compared by means of a paired t-test. Calculated t value was compared with the tabulated t value for 9 degrees of freedom and a significance level of $p=0.05$ ($t=2.26$). The calculated t value (1.00) is lower than the tabulated one, thus the null hypothesis that the methods do not give significantly different values for the mean total As concentration is accepted.

6. Conclusions

A sequential injection system with anodic stripping voltammetric detection for speciation of inorganic arsenic has been exploited. The reagents consumption is minimal. Limits of detection of 1 and 2 $\mu\text{g l}^{-1}$ for As(III) and total As can be achieved. The tubular configuration of the working electrode, in combination with binary sampling strategy, was successfully applied to determine As(III) and total As in groundwater samples without any pre-treatment.

The LODs obtained for As(III) and total As were similar to those reported using continuous flow as sample introduction method. The SI-ASV system uses 0.4 ml of water sample for each determination, which is noticeably smaller than the sample amount reported using other flow methodologies without loss of sensitivity.

The proposed SI voltammetric system is an alternative for cost-effective higher degree of automation. The linearity and response achieved with the system makes it very suitable for arsenic measurements in natural waters with usual concentrations. Samples with higher or lower concentration can also be easily measured by varying the amount of sample aspirated and/or the deposition time.

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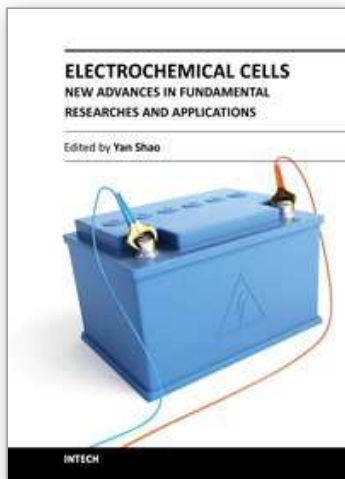
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