ARSENIC SPECIATION STUDY USING X RAY FLUORESCENCE
AND CATHODIC STRIPPING VOLTAMMETRY

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Abstract

Two methods for the determination of total As concentration and its inorganic species by Energy Dispersive X Ray Fluorescence (EDXRF) and Cathodic Stripping Voltammetry (CSV) were developed. The effect of pH on As (III) recovery after precipitation with APDC and EDXRF measurement was studied. Quantification of As was done using the thin layer approach. A reduction of As(V) to As(III) with sodium tiosulphate was necessary in order to determine the total As concentration. The effect of the amount of reducing agent on the recovery was also studied. As(V) concentration was calculated by difference between total As and As(III) concentration. On the other hand, a polarographic method, using the cathodic stripping mode was implemented. As(III) deposition on the electrode was enhanced by addition of Se(IV). Factors affecting As determination (selenium concentration, deposition potential, deposition time) were studied.

Key words: x-ray fluorescence analysis, voltametry, quantitative chemical analysis, stripping, abundance

ESPECIACIÓN DE ARSÉNICO UTILIZANDO LA FLUORESCENCIA DE RAYOS X Y LA VOLTAMETRÍA DE REDISOLUCIÓN CATÓDICA

Resumen

Se desarrollaron dos métodos para determinar la concentración de As total y sus especies inorgánicas mediante fluorescencia de rayos X dispersivo de energía (FRXDE) y la voltametría de redisolución catódica (VRC). Se estudió el efecto del pH sobre la recuperación de As(III) después de su precipitación con APDC y medición por FRXDE. La cuantificación se realizó utilizando la aproximación de capa fina. Para determinar la concentración total de As fue necesario reducir el As(V) a As(III) usando tiosulfato de sodio. Se realizó el estudio del efecto de la cantidad de agente reductor sobre la recuperación. La concentración de As(V) se calculó por diferencia entre los valores de As total y As(III). Se implementó además, un método polarográfico usando la variante de redisolución catódica. Para aumentar la deposición de As(III) en el electrodo se añadió Se(IV). Se estudiaron los factores que afectan la determinación de As (concentración de Se, potencial de deposición, tiempo de deposición).

INTRODUCTION

Arsenic, a well-known toxic chemical, is found in a wide variety of chemical forms throughout the environment and can be readily transformed by microbes, changes in geochemical conditions, and other environmental processes. Its mobility in the environment occurs through a combination of process like biological activities, dissolution of rock and volcanic emissions. Most environmental problems related with arsenic are due to its transport under natural condition, nevertheless, human activity had contributed greatly through mining activity, fuel burning, the use of arsenical pesticides, herbicides and the use of the element as feed additive for animal food [1].

Arsenic in drinking water is of far greater concern. Underground water flowing over arsenic-rich rock may become contaminated with high concentrations of a toxic form of arsenic, which can make its way into private wells and public water supplies. Some adverse health effects have been attributed to chronic arsenic exposure, primarily from drinking water [1,2]. Following the accumulation of evidence for the chronic toxicological effects of As in drinking water, recommended and regulatory limits of many

authorities are being reduced. The WHO guideline value for As in drinking water was reduced to 10 ì g L^{-1}. The US-EPA limit was also reduced from 50 ì g L^{-1} to 10 ì g L^{-1} in January 2001.

It has been long realized that the determination of total arsenic concentration is insufficient in order to evaluate the risk associated with the presence of this element. Arsenic toxicity, bioavailability, transport and distribution in living organism and the environment is dependent on its chemical species present in the sample [3, 4]. Inorganic arsenic is more toxic than the organic species. Among the inorganic, As(III) is considered more toxic than As(V). Thus, additional information about the different species and their concentration is mandatory.

Several methods had been employed for the determination of total arsenic concentration and its chemical species. The most used speciation techniques often involve a combination of chromatographic separation combined with spectrometric detection, including Inductively Coupled Plasma-Atomic Emission Spectrometry (ICP-AES), Inductively Coupled Plasma-Mass Spectrometry (ICP-MS), Atomic Absorption Spectrometry (AAS) and Atomic Fluorescence Spectrometry (AFS) [5-9].

Although, HPLC is the most common and versatile method for separation of arsenic species, it is restricted in its separation capabilities. HPLC requires a large quantity of the mobile phase which in turn contains large quantities of organic solvent which may 1) cause carbon deposits on the sampling cone, 2) cause plasma instability, and 3) quench the plasma.

This results in a decrease in the signal and an increase in noise levels. Also, these coupled techniques are expensive and require trained personals.

Separation techniques based on preconcentration procedures followed by off-line detection of the analytes are valid and inexpensive alternatives for speciation studies. The derivatives of dithiocarbamic acid are known to chelate a large number of metals [10-14]. Ammonium pyrrolidine dithiocarbamate (APDC) is one of the dithiocarbamate derivatives widely used as chelating agent for preconcentration and separation of traces metals from aqueous solution [15]. A relevant feature of dithiocarbamates is that the stability of metal-dithiocarbamate complex depends on the oxidation state of the metal. Thus, the selectivity of APDC for chelating As(III) allows its separation from As(V). Reduction of pentavalent arsenic to As(III) allows the determination of total arsenic concentration; A(V) can be calculated by difference. This preconcentration method is very suitable for XRFDE detection because solids samples can be conveniently measured in such

system, which is a low cost and multielemental technique. Although Neutron Activation Analysis (NAA) has higher sensitivity, you need a reactor facility and the cost of the analysis is high. Other sensitivity techniques like Hydride Generation Atomic Absorption Spectrometry (HG-AAS), ICP-AES, ICP-MS and AFS can be used after dissolution of the species, but this could be a source of contamination and they are also expensive techniques.

Electrochemical techniques, especially stripping voltammetry, have also been used for arsenic determination [9, 16-17]. As(III) can be reduced to the element in acidic solution, deposited onto an electrode and then stripped off using anodic or cathodic stripping voltammetry (ASV and CSV).

There are often problems associated with the use of solid electrodes, such as "memory" effects, limited sensitivity, and poor precision, which makes this approach inconvenient for routine analysis. To avoid these problems, cathodic stripping voltammetry at a hanging mercury drop electrode (HMDE) has been used to determine arsenic, utilising the reaction between arsenic and copper or selenium to form an intermetallic compound that can be pre-concentrated on the HMDE and then stripped cathodically [9, 17-19]. As(V) is electroinactive and must be reduced to As(III) before its determination by CSV.

The aim of this work was to developed a method to determine total arsenic concentration and inorganic As(III) and As(V) concentration in water, based on the selective precipitation of As(III) with APDC followed by its measurement by Energy Dispersed X Ray Fluorescence (EDXRF). A cathodic stripping method was also developed.

EXPERIMENTAL

Apparatus and reagents

The EDXRF spectrometer includes a Si(Li) detector (rξ = 180 eV for Mn-Kα), multichannel analyser (Camberra S30) coupled to a computer. Samples were irradiated with a ^{109}Cd radioisotope annular source (~9 MBq).The fitting of the spectrum was performed with the AXIL program. SAX software was used for the quantification of As in the filters using the thin layer approach.

Voltammograms were obtained with a PA-4 polarographic analyzer interfaced an stand composed by a saturated calomel reference electrode (SCE), a platinum rod auxiliary electrode and a hanging mercury dropping electrode (HMDE) as working electrode. The voltammograms were recorded on a X-Y recorder.

All chemical were reagent grade. As(III) standard were purchased from Fluka (1000 mg L^{-1} for AA analysis). The 1000 mg L^{-1} As(V) stock solution

was prepared by dissolving 0.4223 g $Na_2HAsO_4X7H_2O$ in 1L water. Se (IV) was purchased from Fluka (1000 mg L^{-1} for AA analysis). Working solutions were prepared from these stock solutions daily by appropriated dilution. APDC from SIGMA was used to precipitate As from solutions. Aqueous APDC solutions were prepared fresh daily. Filtrations were done using 0.45 μm nitrate cellulose filter membrane (Whatman).

PROCEDURE

Determination of As(III)

A synthetic solution (1 L) of 50 μg L^{-1} As(III) was adjusted to pH 4 with buffer acetate. After the addition of 5 mL of cadmium solution (100 μg mL^{-1}), As(III) was coprecipitated using 25 mL of 0.25% (w/V) APDC. The turbid solution was gently swirly and filtered, 30 minutes later, through a nitrate cellulose membrane. The filtrate was let dry for 10 minutes and measured by XRFED. Reagent water was used as a blank.

Determination of total arsenic

A reduction step is necessary to reduce all the As(V) to the trivalent state, allowing the determination of total As concentration. One litre of As(V) working solution (50 μg L^{-1}) was acidified to pH=2 and 0.6 g of sodium thiosulphate was added, followed for a waiting period of 15 minutes in order to complete the reaction. Then, the same procedure described above for As(III) precipitation was followed. Similar volume of reagent water was used as a blank and treated the same way.

Determination of As(V)

The amount of As(V) is calculated by difference between the contents of total arsenic and As(III).

Measurement and quantitation

A simplification of the XRF fundamental equation has been used in this work, which relates the characteristic line intensity of the element and its concentration. When the *thin Layer* approach is valid, the peak intensity is straight function of the element concentration, the sample aerial density and the instrumental sensitivity to the given element, and the matrix effects can be rejected.

The resulting aerial density ρd (ρ- density (g cm^{-3}), d- thickness (cm)) of the precipitate, considering a maximal concentration of 100 μg mL^{-1} of the element, 1000 μg mL^{-1} of Cd and a 100% recovery, does not exceed 0.0022 g/cm^2. The mass attenuation coefficient was evaluated for the precipitate composition, and the product $\chi(E_{xi}, E_n)\rho d$

results much lower than *-ln(0.1)*. Therefore the condition for thin layer approach in XRF quantitation is safely observed.
Calculation was carried out using an instrumental sensitivity calibration curve experimentally determined for K_α lines.

Cathodic stripping procedure

10 mL of samples and standards, adjusted to pH=2 with 20% HCl, were placed in the cell and 20 μL of 20 mg L^{-1} Se (IV) solution was added. The solution was purged for 5 minutes with nitrogen. The parameters settings are shown below.

Deposition potential: -0.550 V
Final potential   : -0.900 V
Current range   : 15
Deposition time   : 40s
Amplitude   : 5 mV/
Scan rate   : 5 mV/s

RESULTS AND DISCUSSION

APDC precipitation and XRF measurements

The working conditions used for As(III) precipitation were those reported by Montero *et al*. [20] for the determination of Fe, Co, Ni, Cu, Zn and Pb in rainwater samples, reporting recoveries higher than 94%. Similar recoveries values, about 95%, were obtained for As(III) in the concentration range of 5-100 μg L^{-1}. The relationship between the concentrations of As(III) added and the experimental values is illustrate in figure 1, showing a linear relation.
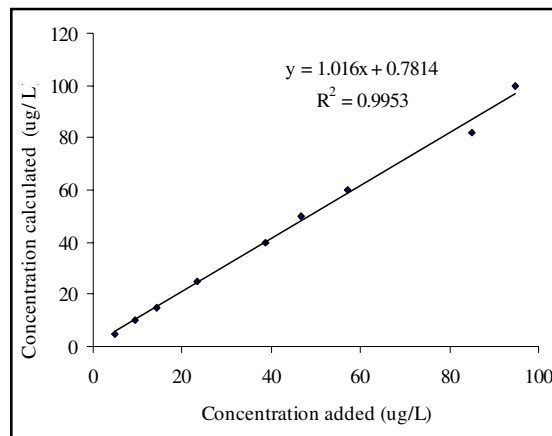

Figure 1. Recovery of As(III).

The influence of the pH (range from 2-6) was studied to select the best condition for quantitative precipitation and the results are illustrate in figure 2. Recovery values were constant until pH= 5, but at pH= 6 recovery decrease drastically. Probably, this is due to the sudden change of redox potential of arsenic at pH values between 5 and 6. Thus,

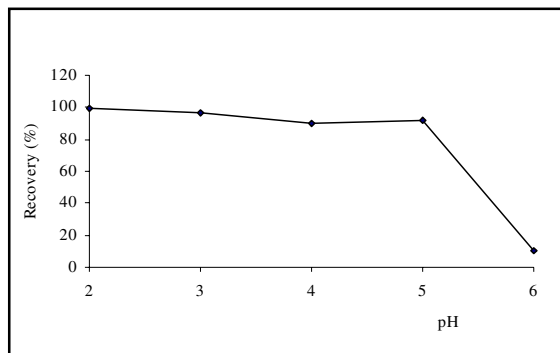appreciable oxidation of As(III) to As(V) occurs, decreasing arsenic precipitation [21].

Figure 2. Effect of the pH on recovery of As(III).

In order to assure that As(V) does not react with APDC, a solution of As(V) 50 μg L^{-1} was treated the same way as As(III). The spectrum obtained from XRFED measurement shows not signal from As. Then it is possible to separate As(III) and As(V) from samples of water.

Because only As(III) reacts with APDC, reduction of As(V) to As(III) is necessary in order to determine total As concentration. Several Compounds had been used for the reduction step, with a variable degree of effectiveness: KI, $Na_2S_2O_3$, $NaHSO_3$, Na_2SO_3, SO_2(g), L-cystein, ascorbic acid, hydrazine, thiourea [15;22,23]. Sodium thiosulphate was often used, combined with other compound or alone, with good results. The experiments of reduction of As(V) solutions, followed by precipitation with APDC and measurement by XRFED showed recoveries between 93-95%. This result was not better when a mix of $Na_2S_2O_3$/KI, at different proportions, were used. This result agrees with those reported by Wai & Mok [15].

At the pH of the solution in the reduction step (pH=2), significant amount of colloidal sulphur is formed because of thiosulphate disproportion reaction [24]. The presence of too high amount of sulphur in the filters could annul the thin layer approach, making impossible the quantification of the analyte. In order to evaluate the influence of the sulphur produced on the recovery values of As, different quantities of reducing agent (0.25-0.8 g)

were assayed for the reduction of As(V). Results (figure 3) showed that the amount of precipitate in the filter, using these quantities of thiosulphate, did not affect the recovery values, which remained almost constant. Thus, using up to 0.8 g of sodium thiosulphate, the sulphur in the filtrates does not annul the thin layer approach. A concentration of 0.6 g L^{-1} of reducing agent was selected for As(V) reduction.

The whole procedure was applied to the determination of total arsenic, As(III) and As(V) concentrations in synthetic solutions. A known volume of the solution was assayed following the procedure for As(III) determination. Another portion of the same volume was treated with sodium
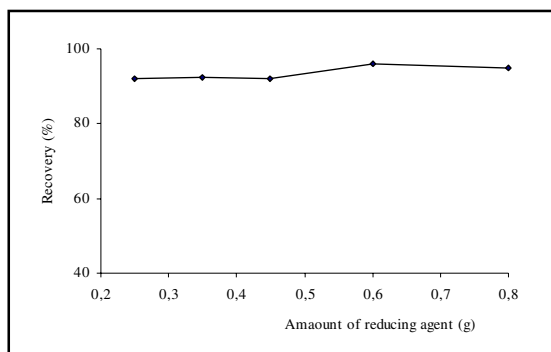

Figure 3. Effect of the amount of reducing agent on As recovery.

thiosulphate before precipitation with APDC, allowing the determination of total As concentration. The difference in As concentrations between the two determinations represents the amount of As(V).

The result of the analysis, expressed as mean ± uncertainty (n= 3, 95% confidence and K=2) for total As concentration and the inorganic species is shown in table 1.

Satisfactory recovery values for both inorganic species (>95%) were obtained. The detection limit, calculated based on Curie criteria [25] and a measuring time of 56500 seconds, was 0.47μg L^{-1}. This value is lower than the maximum admissible concentration in drinking water (50 μg L^{-1}) as stated in NC 92-02 (1985), allowing the monitoring of As in this water. Also, it is

Table 1. Speciation of As(III) and As(V) from a spiked water sample

	As(III) (μg L^{-1})	As(V) (μg L^{-1})	As$_{total}$ (μg L^{-1})
Spike	50.0 ± 0.5	50.0 ± 0.6	100.0 ± 0.8
Experimental value	47.5 ± 4.2	48.2 ± 7.7	95.7 ± 6.5

possible to measure As concentration in unpolluted sea water since the levels of the element in this matrix is about 2 μg L^{-1}. The method can also be apply to water used in hospitals and pharmaceutical industry, which demand low level of heavy metals like Cd, Pb, As.

Cathodic stripping analysis

The arsenic determination by CSV proceeds in to steps: the concentration of As(III) on the HMDE as elemental arsenic, followed by the cathodic stripping to obtain a peak due to the formation of the arsine. The low solubility of arsenic on mercury is a drawback for its determination using this method. The addition of Se (IV) increases the arsenic deposition on the mercury electrode. The formation of the arsine takes place at more negative potential. The behavior of the arsenic in a solution, adjusted to pH=2 with HCL, containing 50 μg L^{-1} As(III) and 40 μg L^{-1} Se(IV) is shown in figure 4. The peak at -0.57 V is due to the formation of hydrogen selenide. At the potential of -0.76 V, the arsenic, deposited on the working electrode as an intermetallic compound with selenium, is reduced and the arsine is formed.
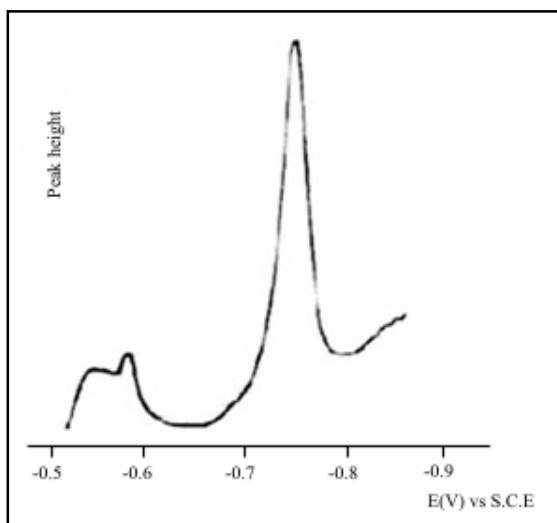

Figure 4. Electrochemical behavior of As(III) in presence of Se(IV).

The deposition potential is critical to ensure the highest sensitivity for the determination of the arsenic. At potentials greater than -0.57 V, the formation of hydrogen selenide proceeds immediately and the deposition of arsenic on the electrode decrease. In order to obtain the desired effect, selenium must be present on mercury. The variation of the As peak height at different deposition potentials (range from -0.4 to -0.6 V) was studied. The As peak height increase until -0.55 V. More negative potential lowered the peak height. Thus, a deposition potential of -0.55 V was choose.

Figure 5 shows the effect of Se(IV) concentration on the cathodic stripping current of As(III). Arsenic peak height increase to about 40 μg L-1 Se(IV). Further increments in the concentration of the selenium did not show effect on the peak of As.
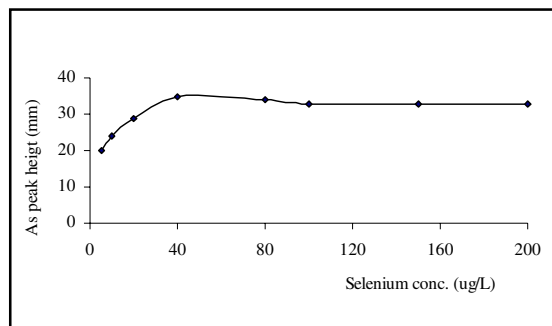

Figure 5. Effect of Se(IV) concentration on the arsenic peak height.

The influence of deposition time on peak height was also studied. The peak height of As increase with the increase in deposition time (40, 120, 240, 360 s). This effect is useful for determination of very low concentration of As, for higher concentration of the analyte, deposition time must be shorter in order to decrease the time of the analysis.

The calibration curve, obtained from solutions of As(III) (concentrations from 20-200 μg L^{-1}) adjusted to pH= 2 and analyzed using a deposition potential of -0.55 V, deposition time of 40 s and 40 μg L^{-1} Se(IV) is shown in figure 6. Detection limit, calculated using the calibration graph under the conditions of the analysis, was 5 μg L^{-1}. This method can be used to monitor the arsenic content in drinking water since it can detect concentration of the element at lower levels than the maximum admissible concentration. The speed of analysis (about 10min/sample) allows the analysis of a great number of samples.

Since the As(III) is the only electro active specie under the conditions used, reduction of As(V) is necessary to determine total As concentration and As(V) is calculated by difference. The procedure of As(V) reduction using sodium tiosulphate was
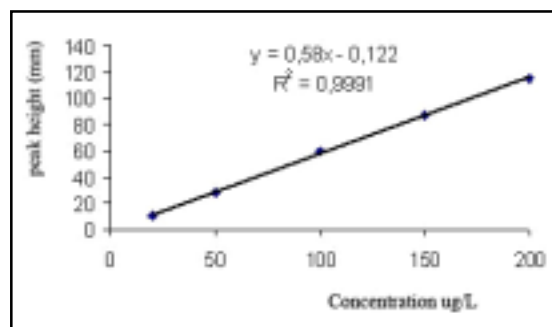

Figure 6. Calibration graph for As (III).

applied in this method for the reduction of 10 mL of solution.

Both methods were applied to samples of drinking water and not As was detected in those samples.

CONCLUSIONS

Selective precipitation with APDC is a simple method for the speciation of As(III) and As(V) in water, allowing the concentration of the element from high sample volumes and its measurement by EDXRF. The low detection limits obtained with this method allows its application to the speciation of As in water with low contents of the element like sea water and in other kinds of water (for pharmaceutical and medical use) that must fulfils very strict conditions related with heavy metal content. The method takes advantages of the multielemental capability, low cost and simplicity of EDXRF as detection method.

Cathodic stripping method is fast, consumes low volume of sample and could be used in the determination of not very low concentration of arsenic.

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