

## Removal of arsenic(V) ions from aqueous media by adsorption on multiwall carbon nanotubes thin film using XRF technique



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### ABSTRACT

A solid phase extraction using multiwalled carbon nanotubes, modified with a tertiary amine, ALIQUAT 336, has been developed as a preconcentration technique for the determination of trace amounts of As(V) in water samples. After “batch-based mode” As(V) adsorption on ALIQUAT 336-Multiwalled carbon nanotubes, determinations were made directly on the solid by X-Ray Fluorescence spectrometry, which reduces the number of reagents used and minimizes the sample handling.

The method herein described combines the advantages of solid phase extraction with the benefits of any X-Ray Fluorescence method associated to the large areas held by the carbon nanotubes, which make them a promising solid sorbent for preconcentration procedures.

The enrichment factor was calculated considering that the thin film obtained from the 100 mL solution of  $1000 \mu\text{g L}^{-1}$  As had a final thickness of 0.04 mm and a final diameter of 16.7 mm, the volume deposited on the pellet was  $0.0088 \text{ cm}^3$ . Thus the preconcentration factor obtained was  $10^4$  fold, which represented a highly satisfactory value for trace analysis by X-Ray Fluorescence.

Satisfactory results were obtained for the determination of arsenic in samples of the standard reference material “NIST 1643e—Trace Elements in Water and drinking water”.

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### 1. Introduction

The presence of arsenic in drinking water has reached calamitous proportions in many parts of the world. Arsenic occurs as both inorganic and organic compounds and its toxicity is strongly related to its chemical form. Consequently, it is essential to perform the speciation of this element in aqueous, geological, and biological matrices (Mazan et al., 2002). Arsenic is a ubiquitous element found in the atmosphere, soils and rocks, natural waters, and organisms. It occurs through a combination of natural processes and human activities (Salaún et al., 2007; Villaescusa and Bollinger, 2008).

Average concentrations of As in freshwater are frequently less than  $1 \mu\text{g/L}$ . Rarely, much higher concentrations are found, particularly in groundwater (Smedley and Kinniburgh, 2002). The biological effects of arsenic depend mainly on the chemical form in which the element is ingested, the route of entry, the dose and the duration of exposure. Inorganic As(III) and As(V) are identified to be more toxic than its organic forms. The arsenic is built up through intake of

food or contaminated potable water (Podder and Majumder, 2016; Maratta et al., 2013). Of the various sources of As in the environment, drinking water probably poses the greatest threat to human health (Seiler et al., 1994). Depending on local availability, drinking water is derived from a variety of sources such as surface waters (rivers, lakes, reservoirs and ponds), groundwater (aquifers) and rain water, which are variable in terms of As risk.

Because of very low concentration of arsenic in environmental and biological samples, sensitive analytical techniques are required. Up to now, a number of analytical methodologies have been developed for the determination of low concentration levels of arsenic, including inductively coupled plasma mass spectrometry (ICP-MS) (Ellwood and Maher, 2002), inductively coupled plasma-optical emission spectrometry (ICP-OES) (Koh et al., 2005; Jitmanee et al., 2005), hydride generation-atomic absorption spectrometry (HG-AAS) (Feeney and Kounaves, 2002; Naykki et al., 2001), hydride generation-atomic fluorescence spectrometry (HG-AFS) (Coelho et al., 2003; Leal et al., 2004), and electrothermal atomic absorption spectrometry (ETAAS) (Pasiás et al., 2013; Qadir et al., 2010). In addition, a number of hyphenated techniques for arsenic speciation, such as ion chromatography coupled with hydride generation-inductively coupled plasma atomic emission spectrometry (Gettar et al., 2000), ion chromatography (Vassileva

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et al., 2001) or high-performance liquid chromatography (Wrobel et al., 2002) coupled to inductively coupled plasma mass spectrometry have also been reported. However, these methods are not sufficiently sensitive for the direct determination of arsenic in water samples. In this context, the development of methods for preconcentration of arsenic species are necessary (Pozebon et al., 1998).

X-ray fluorescence (XRF) spectrometry has also been used for the analysis as well as speciation of As(III) and As(V) (Ali Aldroobi et al., 2013). The main advantage of this technique is its capability for direct analysis of solid and liquid samples, avoiding or at least reducing sample handling to a minimum.

In trace analysis, therefore, preconcentration and/or separation of analytes are necessary to improve sensitivity and selectivity of analysis. Solid-phase extraction (SPE) is the most common technique used for preconcentration of analytes in environmental waters and biological samples, due to its advantages as high enrichment factor, high recovery, rapid phase separation, low cost, low consumption of organic solvents, and the ability of coupling with different detection techniques in the form of on-line or off-line mode (Aranda et al., 2010).

The choice of an appropriate adsorbent in a SPE procedure is a critical factor to obtain full recovery and high enrichment factors. Many sorbents have been used for preconcentration of metal ions (Ahmed, 2008; Ngeontae et al., 2007; Saeed and Ahmed., 2006). In recent years, great attention has been paid to the application of nano-structure materials, especially carbon nanotubes (CNTs). In particular, there have been an increasing number of applications of CNTs in several fields of chemical analysis. The CNTs can be visualized as a sheet of graphite that has been rolled into a tube. These tubes are classified as multiwalled carbon nanotubes (MWCNTs) and single-walled carbon nanotubes (SWCNTs) according to the carbon atom layers in the wall of the nanotubes. Because of their special electronic, metallic, and structural characteristics as well as the unique tubular structures of nano diameter and large length/diameter ratio, CNTs have been exploited in analytical chemistry and other fields (Liang et al., 2008; Tuzen et al., 2008).

The highly developed hydrophobic surface of CNTs exhibits strong sorption properties toward various compounds. Preconcentration SPE-based approaches directed to environmental applications related to the removal of toxic ions from wastewater and industrial processes have been reported. In this context, MWCNTs have been used for the preconcentration of trace amounts of organic materials and the extraction of some ions from environmental samples (Afzali and Mostafavi, 2008; Xu et al., 2003).

The aim of the present study was to develop a method for preconcentration and determination of ultra-trace of As amounts present in water samples through their adsorption on “bach mode” on ALIQUAT 336-MWCNTs which is commercial anionic exchanger extractant, widely used. The determinations were made directly on the solid, by X-ray fluorescence spectrometry, method and large areas held by the carbon nanotubes, making them a promising solid sorbent for preconcentration procedures, direct quantification of the analyte in the solid sorbent; thereby reducing the number of reagents used thus minimizing handling of the sample. The preconcentration factor obtained was  $10^4$  fold, which represented a highly satisfactory value for trace analysis by XRF. Satisfactory results were obtained for the determination of arsenic in samples of the standard reference material “NIST 1643e—Trace Elements in Water and drinking water”.

## 2. Experimental

### 2.1. Reagents and apparatus

Commercial multiwall CNTs were obtained from Sigma–Aldrich, USA, diameter 110–170 nm, longitude 5–9  $\mu\text{m}$ , 90%. Membrane filter papers were Millipore of 0.45 mm pore size.

Stock standard solutions of As(V) with a concentration of  $1000\text{ mg L}^{-1}$  were obtained by dissolving appropriate amounts of  $\text{Na}_2\text{HAsO}_4$  (Merck, Darmstadt, Germany). Working standard solutions were obtained by appropriate dilution of the stock standard solutions.

The extractant, Tricaprylmethylammonium chloride  $\text{CH}_3\text{N}[(\text{CH}_2)_7(\text{CH}_3)_3\text{Cl}]$  (ALIQUAT 336) was purchased from Fluka, Switzerland. Ultrapure water ( $18.1\text{ M}\Omega\text{ cm}$ ) was obtained from Barnstead EASY pure RF water system (Iowa, USA).

All the reagents were of analytical-reagent grade and the presence of arsenic was not detected within the working range.

Measurements were performed with a Philips PW1400 X-ray Fluorescence Spectrometer. The As  $\text{K}\alpha$  line was used for measurements. The conditions were appropriately optimized and are shown in Table 1. The pH of the solutions was measured using an Orion 701-A pH meter with an Ag/AgCl electrode. A M-23 Digital Orbital shaker (Buenos Aires, Argentina), was used for sample agitation.

### 2.2. Activation of the MWCNTs

MWCNTs (25 mg) were added to 30 mL of 2.2 M nitric acid solution, this mixture was sonicated at room temperature for 30 min in ultrasonic bath. After that, the MWCNTs were filtered, washed with distilled water. Then, to eliminate metal oxide catalysts, the MWCNT were dispersed in 60 mL of 6.0 M HCl solution for 30 min under ultrasonic agitation, and then washed with distilled water until the pH was neutral and finally dried in an oven at  $50^\circ\text{C}$ .

### 2.3. Preparation of the loaded MWCNTs

Under the optimized adsorption conditions previously published (Aranda et al., 2010), the anion-exchanger extractant was loaded on the ground MWCNTs. A 50 mg MWCNTs mass was shaken overnight with 40 mL of 5% Aliquat solution in methanol at room temperature. The MWCNTs were then filtered, washed with distilled water, and dried in an oven at  $110^\circ\text{C}$ .

### 2.4. Batch adsorption experiment

A series of standards or sample solutions containing As(V) were transferred into 250 mL beakers and the pH value was adjusted to the desired value with  $0.1\text{ mol L}^{-1}$  HCl or  $0.1\text{ mol L}^{-1}$  NaOH solutions. The volume was made up to 100 mL with ultrapure water and 5 mg of ALIQUAT 336-MWCNTs was added. This mixture was then placed in a shaker for 10 min to facilitate adsorption of the metal ions onto the sorbent.

### 2.5. Preparation of the thin film

Membrane filter papers were Millipore of  $0.45\text{ }\mu\text{m}$  pore size. Different amounts (5, 10, 15, 20, 25 and 30 mg) of the loaded ALIQUAT 336-MWCNTs containing the preconcentrated As(V) were used to prepare the films in order to determine its critical thickness. The filtrations were performed in a filtration apparatus equipped with a vacuum pump (De Vito et al., 2001).

A series of aqueous properly diluted As(V) solutions were preconcentrated. This was done on the ALIQUAT 336-MWCNTs by

**Table 1**  
Main instrument parameters for As determination.

| Parameters                        |   |
|-----------------------------------|---|
| Line                              | As La34°2θ, calibrate with arseniate of Na 33,75° |
| Tube:                             | Rh  |
| Crystal                           | LiF 200 (2d = 4028 Å)                             |
| Colimator                         | F (fine)  |
| Operating conditions of the tube: | 75 kV, 40 mA                                      |
| Mask:                             | 2 (14 mm)   |
| Uper level of the windows (UPL):  | 75%   |
| Lowel level of the windows (LWL): | 25%   |
| Detector:                         | F (flow) or (S) scintillation                     |
| Counting time:                    | 100 s   |

the method described above. The measuring X-ray parameters are shown in [Table 1](#)

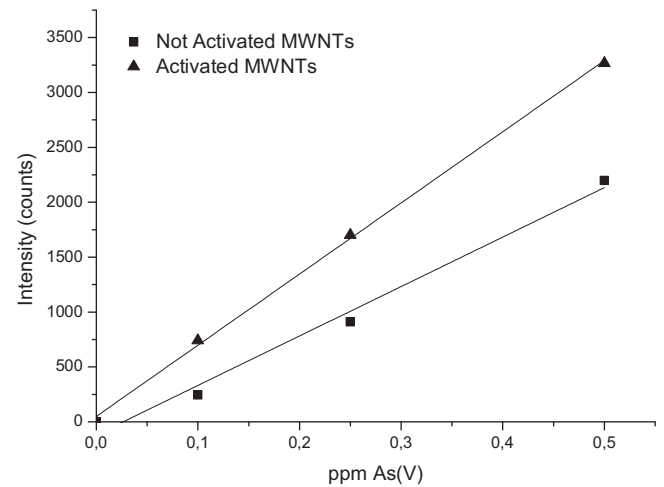
### 3. Result and discussion

#### 3.1. Study of retention of arsenic on activated and not activated MWCNTs

To optimize the experimental parameters of the proposed pre-concentration system, the response of MWCNTs modified with ALIQUAT 336 with and without prior activation was evaluated. With this aim, standard solution of As(V) were preconcentrated and applied following the procedure described above. As shown in [Fig. 1](#), a better response was obtained using MWCNTs with prior activation.

#### 3.2. Effect of shaking time on the sorption

The shaking time is an important factor in determining the possibility of application of ALIQUAT 336-MWCNTs to the extraction of metal ions. In this work, considering the percentage of extraction of As(V) on ALIQUAT 336-MWCNTs, different shaking times (range from 1 to 20 min) were studied. The results indicated that the extraction reaction of As(V) with ALIQUAT 336-MWCNTs was found

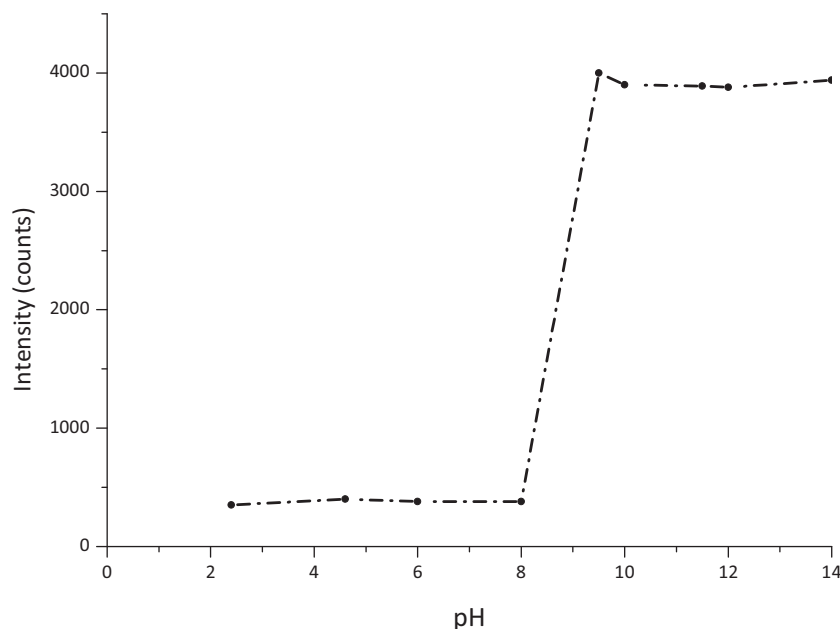


**Fig. 1.** Retention of As(V) on MWCNTs modified with ALIQUAT 336 with and without prior activation.

rapid; the maximum signal was obtained after 3 min of stirring, after that the response stabilized, so a time of 5 min was selected for further studies.

#### 3.3. Effect of the pH on the retention

In order to evaluate the effect of pH, 100 mL solutions containing  $1 \text{ mg L}^{-1}$  of As(V) were adjusted to different pH values with sodium hydroxide or hydrochloric acid. They were mechanically shaken with 5 mg portions of ALIQUAT 336-MWCNTs for 5 min. Then, the ALIQUAT 336-MWCNTs was filtered, washed with distilled water, and later the  $K\alpha$  lines of the analyte were measured by the X-ray Fluorescence Spectrometer. As shown in [Fig. 2](#), the XRF highest intensities of As  $K\alpha$  as function of pH were obtained between pH 9 and 14; therefore, pH 12 was selected for further experiments.



**Fig. 2.** Effect of pH on adsorption of  $1.0 \text{ mg L}^{-1}$  As(V) on ALIQUAT 336-MWCNTs.

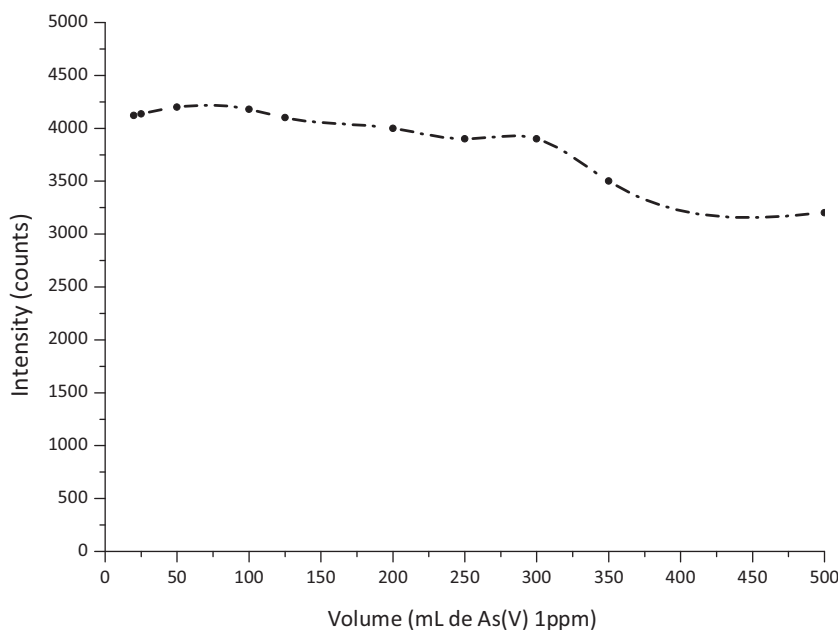


Fig. 3. Effect the sample volume on SPE recovery of As(V).

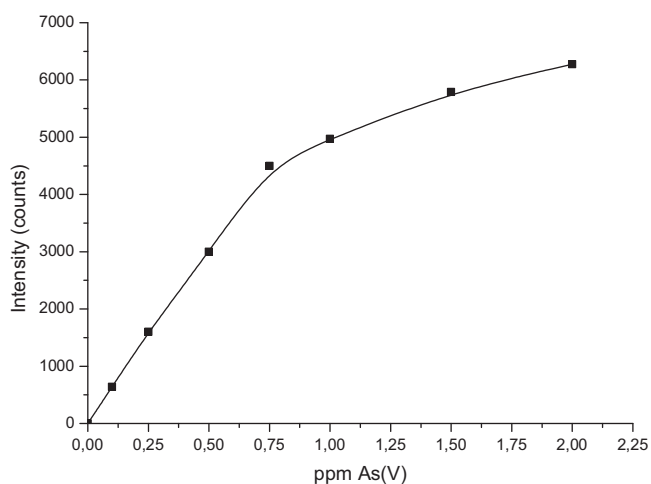


Fig. 4. Retention capacity of As(V) on the ALIQUAT 336-MWCNTs.

#### 3.4. Sample volume and preconcentration factor

Due to the importance of obtaining high preconcentration factors, the influence of the sample volume on the recovery of As on the solid phase was also examined. The results are given in Fig. 3, As(V) ions were quantitatively (>95%) recovered within the volume range of 10–500 mL. Therefore, the 10–500 mL sample solution was adopted as volume range for separation and preconcentration of As.

#### 3.5. Determination of the maximum capacity of retention of the ALIQUAT 336-MWCNTs

Solutions containing different concentrations of As(V) were adjusted to pH 12, shaken and filtered to determine the quantity of analyte that saturated the ALIQUAT 336-MWCNTs material. The As K $\alpha$  line was measured by XRF. In Fig. 4, the XRF intensity of As K $\alpha$  as function of the As(V) concentration is shown. For low As(V) amounts, the concentration was proportional to the As K $\alpha$  intensity. The curve was linear up to 0.75 mg L<sup>-1</sup> of As(V) and became constant at higher As concentrations. The total capacity retention

was 150 mg of As(V) per gram of sorbent material. The percentage of As(V) not retained by the ALIQUAT 336-MWCNTs was determined by inductively coupled plasma optical emission spectrometry in the filtrate. The retained percentage in all cases was greater than 95%.

#### 3.6. Analytical performance

The enrichment factor is defined as  $EF = [QT/QM]/[QT_0/QM_0]$  (Mizuike, 1984), where: QT<sub>0</sub> and QT are the analyte quantities before and after the preconcentration, respectively; and QM<sub>0</sub>, QM are the quantities of the matrix before and after the enrichment, respectively. The enrichment factor was calculated considering that the thin film obtained from the 100 mL solution of 1000 mg L<sup>-1</sup> As(V) had a final thickness of 0.04 mm and a final diameter of 16.7 mm, the volume deposited on the pellet was 0.0088 cm<sup>3</sup>. The preconcentration factor obtained was 10<sup>4</sup> fold, which represented a highly satisfactory value for trace analysis by XRF.

One of the most important features of the use of a preconcentration method is the improvement of the detection limits. A detection limit of 0.1  $\mu\text{g L}^{-1}$  was obtained for aqueous solutions, this was calculated as  $(3/m)(I_b/t)^{1/2}$ , where  $m$ =slope of the calibration curve,  $I_b$ =background intensity (counts/s<sup>-1</sup>) and  $t$ =counting time (s). The precision, expressed as relative standard deviation, for ten replicate determinations at 1000 mg L<sup>-1</sup> As(V) level was 4.0%.

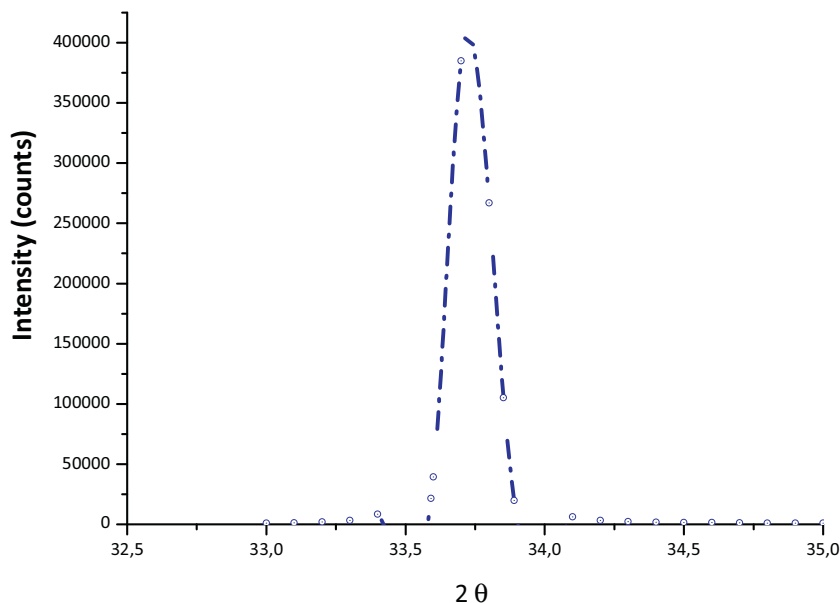
Various preconcentration procedures for the determination of arsenic have been reported, Table 2 shows a comparison among them.

#### 3.7. Recovery study and application to real samples and reference materials

Since a recovery study can be considered as a validation alternative (Beds, 1996), this procedure was applied to the proposed methodology. Thus, 1000 mL of drinking water sample was collected in our laboratory and divided in ten aliquots of 100 mL each. The methodology described above was applied to six portions and the average quantity of arsenic obtained was taken as a base value. Then, increasing quantities of arsenic were added to the other aliquots of sample, after that arsenic was determined by the same method. The recoveries were in the range of 97–102 %.

**Table 2**  
Preconcentration procedures developed for analysis of arsenic.

| Type of samples | Detection Limit ( $\mu\text{g/L}$ ) | Enrichment factor | Sample volume (mL) | Technique  | References                      |
|-----------------|-------------------------------------|-------------------|--------------------|------------|---------------------------------|
| Drinking water  | 0.1                                 | $10^4$            | 100                | XRF        | This work                       |
| Drinking water  | 0.007                               | 45                | 15                 | HG-ICP-OES | Gil et al. (2007)               |
| Drinking water  | 1                                   | 10                | 400                | ETAAS      | Shahlaei and Pourhossein (2014) |
| Drinking water  | 0.005                               | 60                | 1                  | ICP-MS     | Peng et al. (2014)              |



**Fig. 5.** Scanning XRF spectrum of a drinking water sample.

**Table 3**  
Concentrations of As(V) in water for human consumption (95% confidence level;  $n=6$ ).

| Sample | Base ( $\mu\text{g L}^{-1}$ ) | As(V) Added ( $\mu\text{g L}^{-1}$ ) | As(V) Found ( $\mu\text{g L}^{-1}$ ) | Recovery (%) <sup>a</sup> |
|--------|-------------------------------|--------------------------------------|--------------------------------------|---------------------------|
| A      | 1.3                           | 0                                    | $1.3 \pm 0.3$                        | -                         |
| A      | 1.3                           | 2                                    | $3.3 \pm 0.4$                        | 100                       |
| A      | 1.3                           | 4                                    | $5.3 \pm 0.6$                        | 100.0                     |
| A      | 1.3                           | 8                                    | $9.5 \pm 0.4$                        | 102.5                     |
| A      | 1.3                           | 10                                   | $11 \pm 0.8$                         | 97.0                      |
| B      | 59.62                         | 0                                    | $59.62 \pm 3.0$                      | -                         |

A: Drinking water samples collected in our laboratory.

B: Certified value =  $60.45 \pm 0.72 \mu\text{g/L}$ .

<sup>a</sup>  $[(\text{Found} - \text{base})/\text{added}] \times 100$ .

Additionally, the accuracy of the proposed method was evaluated by total arsenic determination in certified reference material NIST CRM 1643e, with an As content to  $60.45 \pm 0.72 \mu\text{g/L}$  and a Density equal to  $1.016 \text{ g/mL}$  at  $22^\circ\text{C}$ . The results are shown in Table 3.

The other elements present in the sample did not show spectral interferences in the determination. A full scan using the As  $K\alpha$  line was obtained and no spectral interferences were observed (Fig. 5).

#### 4. Conclusions

The methodology proposed enabled separation and determination of As(V) in drinking water samples at  $\mu\text{g L}^{-1}$  levels. A  $10^4$ -fold EF was obtained furthermore, the method developed here is a promising method for As(V) determination which joints the advantages of the minimal reagent employment, feasibility, low cost, and sensibility. The high enrichment factors obtained encouraged us to propose this preconcentration methodology as a worthy tool for trace analysis by XRF analysis, which enables improvement of the detection limits and determination of trace elements with high precision.

Although the preconcentration procedure of the proposed methodology was similar to previously reported (Aranda et al., 2010). The ALIQUAT 336-MWCNTs based procedure showed better selectivity, detection limit, pH range applicability, capacity, reproducibility, accuracy and no need of consumption of organic solvents to the arsenic separation—preconcentration methods in bibliography.

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