

A quartz tube atomizer with tungsten coil: a new system for vapor atomization in atomic absorption spectrometry

Anderson Schwingel Ribeiro, Marco Aurélio Zezzi Arruda and Solange Cadore*

Instituto de Química, Universidade Estadual de Campinas, CP 6154, 13083-970 Campinas, SP, Brazil. E-mail: cadore@iqm.unicamp.br

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A quartz tube atomizer with a tungsten coil (QTAW) is described for the determination of arsenic in a flow injection hydride generation system. The flow injection system includes a Nafion[®] membrane that continuously dries the gaseous species, allowing removal of 4.2 mg min⁻¹ of water, corresponding to an efficiency of 92.7%. The application of this system to the determination of arsenic, using the optimized conditions, shows considerable stability with time, without loss of sensitivity, and it was possible to obtain a calibration curve with a wide range (up to 500 µg l⁻¹), with $R^2 = 0.9998$, a limit of detection of 1.5 µg l⁻¹ and an analytical frequency of 60 determinations per hour. The determination of arsenic in samples of mineral and sea-waters, sediment and biological materials, shows good accuracy and precision between the results obtained and the certified values for the recovery of arsenic, with RSD values less than 6%.

Introduction

Atomic absorption spectrometry (AAS) is a well established and well known technique that has been used for the determination of many elements using flame or electrothermal atomization.^{1,2} In 1969, Holak³ used the concept of hydride generation to determine arsenic by AAS. When the acidified sample, containing arsenic, was put in contact with a reducing reagent the generation of the volatile hydride, AsH₃, occurred. Some advantages of the generation of volatile hydrides are: the analyte is separated from the matrix, resulting in better precision; the selectivity is enhanced due to the reduction of interfering species; using a batch system it may be possible to have enrichment of the analyte; the limits of detection (LOD) are improved, allowing the determination of trace-elements and environmental studies; and the systems can be automated, reducing the amounts of reagents and increasing the transport efficiency of the analyte to the atomizer.⁴⁻⁶

A quartz tube atomizer (QTA), heated in a flame or electrically, is generally used for the atomization of hydride forming elements, reaching temperatures of about 700–1100 °C. QTA allows a longer residence time of the analyte in the spectrometer optical path, enhancing the sensitivity with low signal noise and excellent LOD. Sometimes, however, QTA may be susceptible to some disadvantages: there are some interferences associated with the atomization step and its surface may be modified along with time, leading to losses in sensitivity and repeatability of the analytical signals. To minimize such inconveniences, Dedina and Matousek⁷ have proposed the use of a QTA with multiple micro flames, which increases the sensitivity of the analysis, extends the linear calibration range and may tolerate higher levels of interferences.

Recently, Luna *et al.*⁸ have studied the generation of volatile species such as Ag, Au, Cd, Cu and Zn for atomic absorption spectrometry and found that low sensitivity attributed to the low QTA temperature hindered the determination of all the metals. Higher temperatures could overcome this problem, since the process of vapor generation is efficient, as demonstrated for Au, reaching 92%.

An alternative to graphite tubes is the use of an electrothermal atomizer with a tungsten coil (ETAWS). This atomizer has been used for many different samples, aiming at the

determination of different species.⁹⁻¹² Among the advantages of ETAWS are: (a) low cost of the tungsten coil, due it is wide use in overhead and photographic projectors; (b) low electrical consumption, about 150 or 250 W (the filament operates at 15 V and 10 A or 25 V and 10 A, respectively); (c) attainment of temperatures up to 3200 °C, changing according to the applied voltage; (d) lack of memory effects, due to the non-porous surface of the filament; (e) no need of a refrigeration system; and (f) no formation of refractory carbide, which allows determination of some of the carbide-forming elements (like lanthanides).

The use of a tungsten coil for ETAWS was proposed in 1972, by Williams and Piepmeier,¹⁰ who used commercial filaments. At that time, however, there was no equipment for the adequate measurement of short signals so that this work did not attract the attention of other researchers. Only in 1986, Berndt and Schaldach⁹ proposed an open system operating with a tungsten coil. The results were good enough to convince the scientific community of the potential of this technique. Since then, the tungsten coil as an atomizer for ETAWS has been successfully used by several different authors. Thus, this technique has been widely used for the determination of Cd^{11,13} and Pb¹³ in biological material, Ba¹⁴ in water samples and Se,¹⁵ using iridium as a permanent modifier for the filament. It may also be used coupled to some preconcentration systems, either in mini-columns¹⁶ or electrochemically,¹⁷ when flow systems are used.

The use of a rhodium-coated tungsten coil for *in situ* trapping of selenium in a flow injection hydride generation manifold was recently described by Barbosa *et al.*¹⁸ The selenium hydride flows through a capillary quartz tube, reaching the tungsten coil surface modified with rhodium. After 60 s of trapping an enrichment factor of 200 was obtained.

Cankur *et al.*¹⁹ described the on-line trapping and preconcentration of bismuth on a tungsten coil heated at 270 °C. By increasing the temperature to 1200 °C the analyte was released to an externally heated silica T-tube and determined by AAS.

In recent instrumental advances, the use of a tungsten coil associated to multielement²⁰ or portable²¹ equipment that operates with a battery as power supplier and a diode laser as radiation source²² have been described.

The aim of this work was the development and application of a new quartz tube atomizer with a tungsten coil (QTAW) for hydride generation atomic absorption spectrometry in a flow injection system. Quartz tube atomizers are externally heated and the central region, where the radiation passes, is cooler than the quartz surface. With the use of QTAW, the temperature inside the atomizer is higher due to the tungsten coil, allowing some improvements in the determination of volatile species. The system was optimized concerning the parameters involved in hydride generation, the flow system and the characteristics of the tungsten coil. The performance of the proposed system was evaluated for the determination of arsenic in water, sediment and biological materials.

Experimental

Instrumental

All measurements were carried out with an AAnalyst 300 (PerkinElmer, Norwalk, CT, USA) atomic absorption spectrometer equipped with an arsenic electrodeless discharge lamp and a deuterium background corrector under the following operating conditions: wavelength, 193.7 nm; slit-width, 0.7 nm; current, 380 mA.

A closed microwave system (Qwave-3000, Questron Corporation, USA), equipped with temperature and pressure sensors and a magnetron of 2450 MHz with nominal power of 1200 W, was used for sediment sample preparation while a muffle (Forlabo Ltd., SP, Brazil) was used for the treatment of the biological samples.

Four types of filaments were evaluated: (a) 64633HLX, 15 V, 50 W (Osram GmbH, Germany); (b) 64655HLX, 24 V, 250 W (Osram); (c) T3.15DLL, 20 V, 150 W (Osram Sylvania, Brazil); and (d) T3 Halogen, 20 V, 150 W (Osram Sylvania). The temperature of the tungsten coils was measured by an Ultimex-Infrared Thermometer optical pyrometer (Incon, USA) equipped with a Close-up VX-CL1 lens.

Reagents

Analytical reagent grade materials were used for all the experiments. Deionized water (18.2 M Ω cm) obtained from a Milli-Q water system (Bedford, MA, USA) was used throughout. Nitric and hydrochloric acids were distilled with a quartz sub-boiling system (Marcone, Piracicaba, Brazil) before being used for sample digestion.

The arsenic standard solution was prepared by dissolving 1.0000 g of As₂O₃ (C. Erba) in 20% (w/v) NaOH with the addition of 2 drops of phenolphthalein. This solution was neutralised with 20% HCl (v/v), diluted to a final volume of 1000 ml with 1 mol l⁻¹ HCl solution and stored in polyethylene bottle, under refrigeration. Adequate dilutions were made, whenever necessary, with 1 mol l⁻¹ HCl.

Solutions of sodium tetrahydroborate were prepared by dissolving NaBH₄ powder (Nuclear) in 0.05 mol l⁻¹ KOH and stored in plastic bottles, under refrigeration. The solution is stable for about 2 weeks, with no loss of the observed absorption signal.

A Nafion[®] 117 membrane (Aldrich, no. 27,467-4) was used to dry the gas formed in the system before it reached the tungsten filament.

Solutions of interfering ions were prepared by the dissolution of appropriate salts or metals in acid or de-ionized water.

The proposed methodology was applied to the determination of arsenic in five certified reference materials (CRM 422—BCR Cod muscle; CRM 278R—BCR Mussel tissue; SRM 1566a—NIST Oyster tissue; CRM 414—BCR Plankton; and CRM 320—BCR River sediment) as well as in water samples (mineral water and sea-water).

Sample preparation and measurements

Water. Sea-water was collected in Ponta do Lessa (Florianopolis, SC, Brazil), filtered with quantitative paper (Whatman), acidified with 1 mol l⁻¹ HCl and stored in a refrigerator before use.

Mineral water was purchased in the local market, acidified with 1 mol l⁻¹ HCl and stored in a refrigerator before use.

When necessary, the samples were enriched with known amounts of arsenic and their recoveries were determined.

Biological samples. Conventional procedures, including acid digestion in Teflon[®] bombs, microwave oven and dry ash calcination, were used for arsenic determination. When organo-arsenic compounds, such as arsenobetaine, were present more severe conditions were required. In this study the method suggested by Leblanc and Jackson²³ was modified: 250 mg of biological sample and 1.5 g of Mg(NO₃)₂ were weighed in a 50 ml beaker, 10 ml of concentrated HNO₃ were added and the solution was heated almost to dryness. The resulting ash was treated in muffle furnace at a temperature of 200 °C, gradually increased up to 450 °C (50 °C per 30 min). This temperature was maintained for 30 min. The white ash obtained was transferred with 4.2 ml of concentrated HCl and water was used to obtain a volume of 50 ml.

Sediment. For each replicate, 250 mg of the sediment was transferred to a microwave oven digestion flask and 5 ml of *aqua regia* (3:1 concentrated HCl:concentrated HNO₃) were added. After 20 min 2.5 ml of HF were added and the flask was closed and introduced into the oven, allowing the complete decomposition of the material using the program described in Table 1. The final solution was heated at 75 °C on a hot plate and then quantitatively transferred to a 50 ml flask with 1 mol l⁻¹ HCl. To guarantee the presence of all arsenic as As(III) biological and sediment samples for analysis were treated by the method proposed by Nielsen and Hansen.²⁴ 6.0 ml of the decomposed solution were transferred to a 10 ml flask containing 200 mg of KI, 400 mg of ascorbic acid and 2.8 ml of concentrated HCl. The volume was adjusted with water and the solutions were introduced to the system for absorbance measurements.

Flow injection system. Fig. 1 shows the FI system consisting of a merging-zones manifold coupled to the QTAW. Loops, reaction coils and transmission lines were of Teflon[®] tubing (Masterflex[®], 0.75 mm id). A proportional injector²⁵ made from acrylic was used for the introduction of solutions into the system. Samples, reagents and waste solution were aspirated with an eight-channel peristaltic pump (Ismatec[®], Zurich, Switzerland) through Tygon[®] tubes (Masterflex[®], EUA) with appropriate flow rates for each solution.

Defined volumes of sample and of reducing reagent were introduced into adequate carrier flows and, after mixing at the confluence point, they were introduced into the reaction coil. The generated hydride was separated from the liquid phase in the gas-liquid reactor-separator (GLS). The hydride was transported with a controlled gas flow rate throughout the gas drying unit (DN) and then introduced into the QTAW for hydride atomization. The carriers for sample and reducing reagent were 0.3 mol l⁻¹ HCl and a less concentrated solution

Table 1 Microwave oven program for the digestion of river sediment

Step	Power/W	Time/min
1	200	3
2	400	5
3	600	5
4	700	20
5	80	2

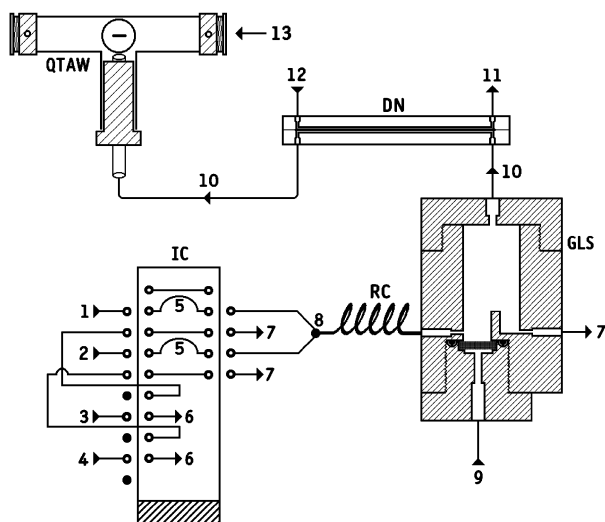


Fig. 1 Flow diagram of the proposed system. IC: injector–commutator; RC: reaction coil (60 cm long, 0.8 mm id); GLS: gas–liquid separator; DN: gas drying unit; QTAW: quartz tube atomizer with tungsten coil (filament A: 4.5 V); 1: 0.3 mol l⁻¹ HCl (4.5 ml min⁻¹); 2: 0.3% w/v NaBH₄ in 0.5% w/v KOH (4.5 ml min⁻¹); 3: sample; 4: 0.7% w/v NaBH₄ in 1.0% w/v KOH; 5: injection volume (1000 µl); 6: recirculation; 7: waste; 8: confluence point; 9: argon (250 ml min⁻¹); 10: gas flow; 11: humid gas; 12: argon (400 ml min⁻¹); 13: light beam of AAS.

of NaBH₄, which continuously generates the hydrogen that takes part in the atomization process of the analyte and also provides the reducing atmosphere required for the optimized operation of the QTAW. The tungsten coil is connected to a power supply (Anacon Científica, SP, Brazil) through a copper electrode and a multimeter (UNI-T[®]), used to control the heating of the tungsten coil. It can be kept on constantly, allowing an adequate isothermal environment for the studied system. Under these conditions, the filament can be used for more than 130 h.

Gas–liquid reactor–separator. A stripping-type gas–liquid separator was manufactured with acrylic, resulting in three internal compartments, as shown in Fig. 2. The separation of

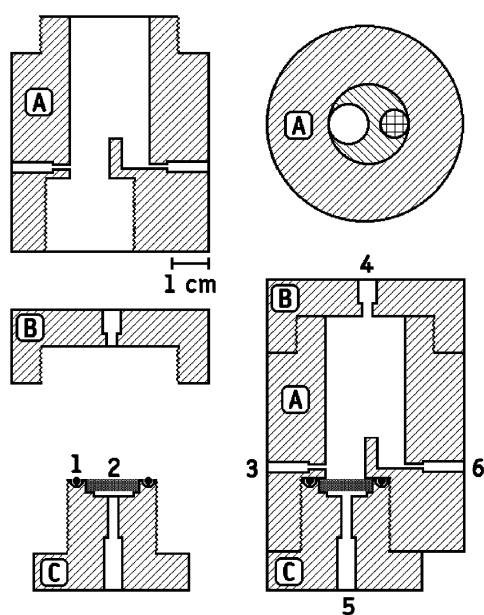


Fig. 2 Stripping-type gas–liquid reactor–separator used in the proposed system. A: Central block; B: upper cover; C: lower cover; 1: O-ring; 2: sintered glass; 3: sample inlet; 4: gas outlet; 5: gas inlet; 6: waste.

gaseous hydride from the liquid fraction occurs in the first compartment and the gas enters into the second compartment, which has a larger internal diameter. This geometry permits a more efficient separation of the hydride, allowing high drainage efficiency of the liquid fraction and avoiding losses of the gaseous fraction. Using this gas–liquid separator, which has an inner volume of 10 ml, it is possible to work with a total flow rate up to 15 ml min⁻¹ when an efficient drainage of waste solution is used, without passage of any liquid fraction through the gas drying unit. Under these conditions the water vapour may be efficiently removed from the gas fraction before being introduced into the QTAW.

Gas drying unit. The gas drying unit was based on the work of Sundin *et al.*,²⁶ where a commercial system with a Nafion[®] membrane in a tube form (30.5 length and 1–2.2 mm id) was used. In this study the gas drying unit was manufactured with two acrylic blocks, with 1 mm deep channels engraved for the passage of the gas. Between them a Nafion[®] membrane (3.2 × 5.8 cm) (Fig. 3) was placed. The gas coming from the GLS enters through one side of the gas drying unit and the water vapor is retained/eliminated due to the presence of a N₂ or Ar stream flowing in counter current. The dried gas (hydride and hydrogen) is then transferred to the QTAW. This membrane may be used for more than 1 year without changing if it is regenerated, after 1–2 months of constant use, with a 15% v/v H₂SO₄ solution for 48 h, washed five times with deionized water, dried for 1 h at 70 °C and finally degassed with a 10⁻⁴ mm Hg vacuum system.

QTAW

The QTAW was manufactured with quartz, where three tubes are connected, two of them at a 90° angle between themselves and the optical axis, as can be seen in Fig. 4. The connections were made with Teflon[®] and quartz windows were put on the extremities of the tube in order to avoid the presence of oxygen in the atomizer, which would lead to filament oxidation and, consequently, to a reduction in lifetime. The presence of two little orifices in the Teflon[®] connection allowed the exit of the gas and the maintenance of a reducing environment inside the atomizer, even at low gas flow rates, leading to the perfect

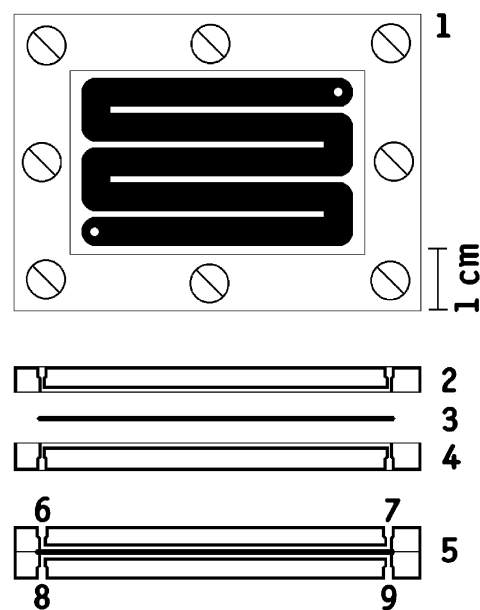


Fig. 3 Gas drying unit. 1: Acrylic block with 1 mm deep channel; 2: upper block; 3: Nafion[®] membrane; 4: lower block; 5: system closed like a sandwich; 6: entrance of dried gas (Ar); 7: exit of humid gas; 8: entrance of humid gas; 9: exit of dried gas (AsH₃ + H₂).

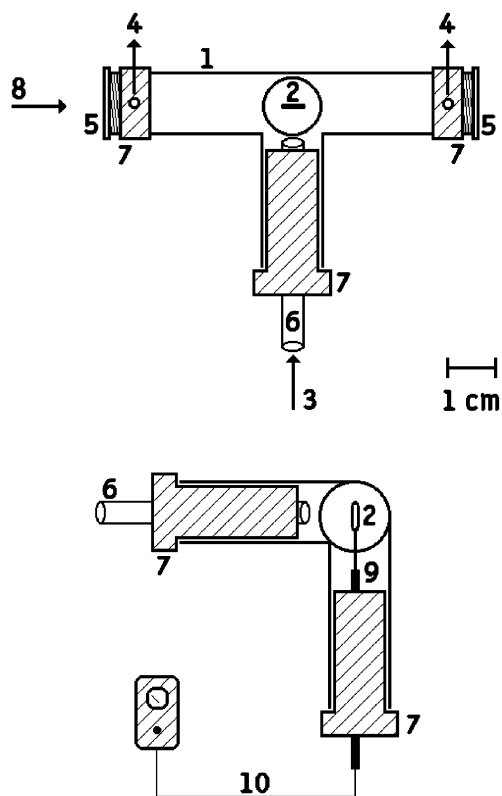


Fig. 4 Quartz tube atomizer with tungsten coil used as the electro-thermal atomizer for the on-line atomization of AsH_3 . 1: Quartz cell; 2: tungsten coil; 3: gas inlet; 4: gas outlet; 5: quartz window; 6: quartz tube; 7: Teflon[®] fitting; 8: light beam; 9: copper electrode; 10: power supply.

performance of the tungsten filament. The atomizer is positioned over a block manufactured from aluminium and Teflon[®], placed in the optical path of the spectrometer. If necessary it is easy to change the filament since it is connected to the copper electrode by screws. Fig. 5 shows the different types of tungsten coils studied in this work.

The QTAW was cleaned with a 10% v/v HF solution for 15 min. A 10% v/v HNO_3 solution was used for 12 h for the quartz tube window. After drying, the atomizer and the windows were treated with 5% v/v dichlorodimethylsilane for 2 h to avoid recombination of gaseous species with the atomizer.

Results and discussion

Preliminary studies were carried out in order to evaluate the behaviour of the QTAW by using the conditions described by Cadore and Baccan.⁴ For the determination of arsenic the

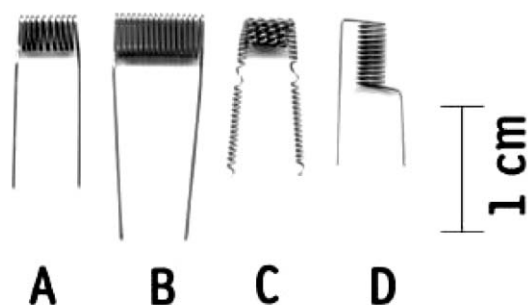


Fig. 5 Pictures of the tungsten coils used in QTAW. A: 64633HLX; B: 64655HLX; C: T3.15DLL; D: T3Halogen. Characteristics described in the text.

optimized conditions for the proposed system were selected taking into account the studies discussed below. Each result represents the mean of at least three measurements.

In order to eliminate the humidity of the system, which could lead to burning of the filament in few minutes of work (5–10 min, at most), a gas drying unit (DN) was introduced before the atomizer. It consisted of a Nafion[®] membrane that retains the H_2O vapor without loss of the gaseous hydride. To evaluate its efficiency the water vapor coming from it, and that from the gas–liquid separator, was collected into separate glass columns filled with calcium chloride, the mass of water was weighed and the efficiency of the DN was calculated as being higher than 92%. This result, obtained for 60 min of continuous use, was similar to that obtained by Sundin *et al.*²⁶ using a commercial system.

(a) Effect of the temperature of atomization

The first parameter considered in this study was the effect of temperature on arsine atomization that occurs in the atomization cell containing the tungsten coil. The temperature at the surface of the filament is a function of the applied voltage and may influence the internal environment of the cell once it is closed with the quartz windows. The behaviour of arsine atomization for different values of voltage obtained with four different filaments was evaluated, with reference to their geometry and characteristics. Different performances were expected, and Fig. 6 shows that an increase of the applied voltage leads to an increase in the analytical signal, up to a maximum, after which it decreases, for all the filaments. The maximum sensitivity using filament A was obtained with 4.5 V for solutions containing from 30 to $160 \mu\text{g l}^{-1}$ of arsenic. As the signals were shown to be independent of the arsenic concentration, the studies for filaments B, C and D were made using only $100 \mu\text{g l}^{-1}$ arsenic solution. For filaments B and C the best signals were obtained with 6.5 V, while a voltage of 7.0 V was more suitable when filament D was used.

An optical pyrometer was used to determine the temperature on the filament, as a function of the applied voltage, for all the filaments evaluated. Considering that the best signals obtained with filaments A, B, C and D are related to the voltages of 4.5, 6.5, 6.5 and 7.0 V, respectively, it is possible to note from Fig. 7 that this corresponds to an atomization temperature of $1610 \pm 50 \text{ }^\circ\text{C}$ for all the filaments. This temperature is considerably higher than that obtained with QTA and it may represent a great advantage mainly regarding interference effects. When a quartz tube atomizer is used for arsine determination the atomization temperature is about $900 \text{ }^\circ\text{C}$.⁸ Otherwise, the

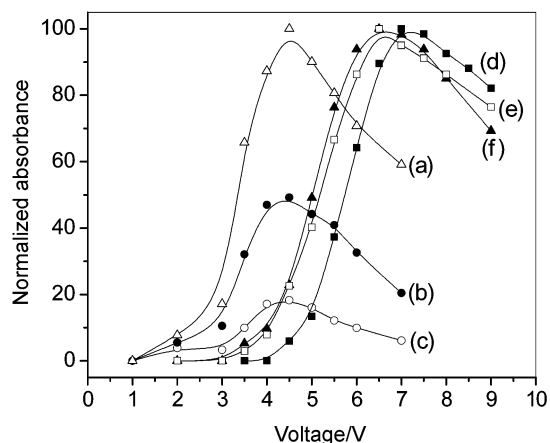


Fig. 6 Influence of the voltage applied to the tungsten coil on the sensitivity for arsenic. (a) Filament A— $160 \mu\text{g l}^{-1}$ As; (b) filament A— $80 \mu\text{g l}^{-1}$ As; (c) filament A— $30 \mu\text{g l}^{-1}$ As; (d) filament D— $100 \mu\text{g l}^{-1}$ As; (e) filament C— $100 \mu\text{g l}^{-1}$ As; (f) filament B— $100 \mu\text{g l}^{-1}$ As.

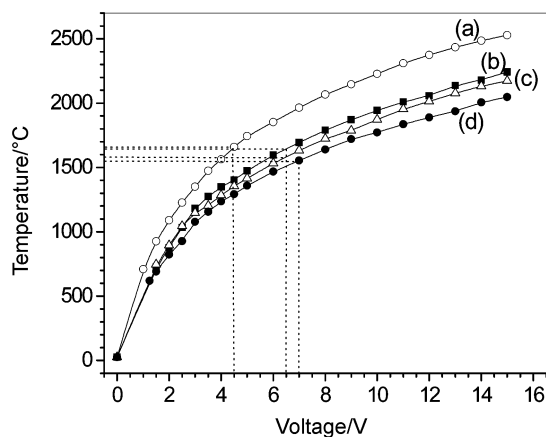


Fig. 7 Effect of applied voltage of the QTAW on the temperature at the coil surface. (a) Filament A; (b) filament B; (c) filament C; (d) filament D.

temperature in the gaseous phase (3 mm above the coil) for filament A decreases 35% and 60% for applied voltages of 15 and 3 V, respectively.¹² This suggests that arsine atomization probably occurs in the regions closest to the filament but not exactly on its surface. This may justify, together with the geometry and characteristics of the tungsten filaments, some temperature fluctuations depending on the applied voltage.

Considering the results obtained it is possible to conclude that any one of the filaments may be used for arsenic determination. For the remainder of this study, filament A was selected for the optimization of the parameters involved in FI and HG techniques, due to its easy commercial availability.

(b) Effect of acid concentration and sodium tetrahydroborate concentration

The presence of HCl provides an adequate medium for the formation of the hydrogen required for arsine generation and its atomization.²⁷ It was observed that the efficiency of arsine generation was not affected by the hydrochloric acid concentration for values between 0.2 and 2.5 mol l⁻¹, but considering the generation of hydrogen in the FI system, it is more convenient to work with low concentrations of hydrochloric acid as a carrier. Concerning the sample treatment, the use of HCl 1.0 mol l⁻¹ was considered adequate. The presence of other acids in the system was also investigated. These are usually used in the sample treatment step and it was observed that the analytical signals decrease in the presence of sulfuric acid (concentrations higher than 1.5 mol l⁻¹) or nitric acid (concentrations higher than 0.2 mol l⁻¹). Although these are present in low concentrations they have oxidizing characteristics which may oxidise As(III) to As(V), interfering in its reduction to arsine. A minimum volume of these acids must be used when sample treatment is required, in order to facilitate their removal from the final solution and to avoid their interferences in arsenic determinations.

As well as the acid medium, an adequate concentration of the reducing reagent (NaBH₄) will guarantee the formation of the hydrogen radicals that will be used in the process of generation and atomization of arsine. As can be seen in Fig. 8, the analytical signals increase with the concentration of sodium tetrahydroborate up to 0.7% w/v. Afterwards they remain practically constant, for different concentrations of arsenic. For lower concentrations of reducing reagent the amount used in this study was not enough for the complete reduction of arsenic. Otherwise, concentrations higher than 0.7% w/v generate an excess of hydrogen and water vapor that can be transferred to the atomization cell. Using QTAW, the damage is more pronounced than in the case where a QTA is used,

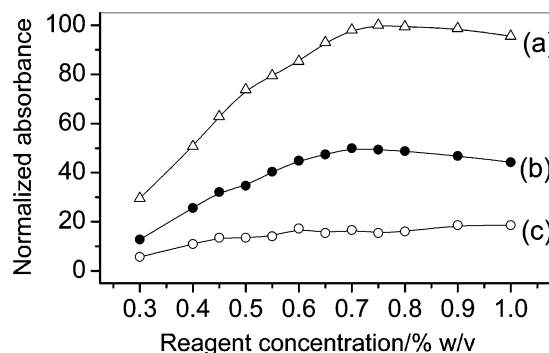


Fig. 8 Effect of the amount of NaBH₄ on hydride generation with different concentrations of As. (a) 160 μg l⁻¹; (b) 80 μg l⁻¹; (c) 30 μg l⁻¹.

because water vapor may cause burning of the filament. In this case the efficiency of the gas drying unit may be a critical parameter. The presence of H₂ in the QTAW is essential, for two reasons: it is well known and established that it takes part in the process of arsine atomization²⁸ and, according to Berndt and Schaldach,⁹ when a mixture of 90% Ar and 10% H₂ is used as purge gas, it is possible to observe an increase in sensitivity for some elements. This mixture (90% Ar + 10% H₂) allows a reducing environment avoiding the recombination between the analyte and tungsten oxides, in the gaseous phase, which would affect the atomization process. On the other hand, the presence of H₂ is necessary to prevent oxidation of the tungsten coil.

As a result of these studies it was possible to select the carrier for the sample as a 0.3 mol l⁻¹ HCl solution and for the reducing reagent, a diluted solution (0.3% w/v) of NaBH₄ prepared in 0.5% w/v KOH. Under these conditions a reducing environment was obtained and the filament could be operated for a long period of time without any damage.

(c) Reaction coil and injection volume

The time necessary for the conversion of arsenic into arsine to occur is determined by the length of the reaction coil, where analyte, acid and sodium tetrahydroborate are in contact. In order to establish this time, different lengths of the reaction coil were evaluated, for arsenic concentrations of 30, 80 and 160 μg l⁻¹. It was observed that the analytical signals were not affected by the length of reaction coil, considering the range from 20 to 80 cm, indicating that arsenic is rapidly converted into arsine. Yamamoto *et al.*²⁹ have already described this behaviour for As(III), while Sturman³⁰ reported an increase in sensitivity with the length of the reaction coil. A reaction coil of 60 cm was selected for the determination of arsenic, due to the physical arrangement of the system, but it is also possible to work with 40 cm, which would enhance the analytical frequency.

When the injection volume of sample and reducing reagent changed from 200 to 1000 μl an increase in the analytical signals was observed and this effect was more pronounced for more concentrated solutions of arsenic. An improvement in sensitivity was obtained for volumes higher than 600 μl. The analytical curves for different injection volumes of NaBH₄ and As showed the following slopes: 0.00061, 0.00100 and 0.00110 (μg l⁻¹)⁻¹ for 200, 600 and 1000 μl, respectively. According to these results, an injection volume of 1000 μl was considered suitable for the determination of arsenic.

(d) Effect of carrier gas flow rate

As previously stated, adequate performance of the tungsten coil requires a reducing environment consisting of 90% Ar+10% H₂. Considering that hydrogen is generated in the reaction coil and it is transferred to the atomizer using a carrier

gas, it is advisable to select argon as a carrier in order to obtain this environment. Flow rates of Ar less than 80 ml min^{-1} showed a lack of detectability and repeatability. An increase of the gas flow rate enhanced the analytical signals but, above 250 ml min^{-1} , a higher injection frequency associated with dilution of the arsine decreased the temperature inside the atomizer and consequently the analytical signals. Thus, an argon flow rate of 250 ml min^{-1} was chosen.

(e) Effect of different tungsten coil in analytical curve

The use of a tungsten coil as atomizer for ETA is already well established, because of characteristics such as chemical resistance, melting point temperature ($3400 \text{ }^\circ\text{C}$), low vapor pressure, as well as its low price and commercial availability; filaments A and B (Fig. 5) are generally used for this purpose.

Using the conditions described in Fig. 1 and the voltages resulting from the discussion of Fig. 6, the behaviour of different filaments for the determination of arsenic was studied for concentrations of $10\text{--}360 \mu\text{g l}^{-1}$. For all the filaments a linear response and very close LODs were obtained, with small differences between them, as shown in Fig. 9. Apparently, the geometry of the tungsten coil does not affect the QTAW. The main reason for this behaviour is because the analyte is transferred to the atomizer in the vapor form and the atomization is carried out in an isothermal environment. In this way, it was possible to confirm that each one of the investigated filaments may be used for the determination of arsenic with the proposed system.

(f) Effect of reagent flow rate on the calibration curve

Taking in account the fact that the reagent flow rate may influence the determination of arsenic using FI-HG with QTAW, the effect of the carrier flow rates of the FIA system (HCl and NaBH_4) on the arsenic signal was determined. The absorbance was measured when the flow rates of reagents were 3.0 , 4.5 and 6.0 ml min^{-1} . Fig. 10 shows the resulting effect on the analytical curves obtained with arsenic concentrations from 5 to $1000 \mu\text{g l}^{-1}$. As can be seen, an increase in the reagent flow rate leads to a better slope of the analytical curve and a consequent improvement in LOD, associated with a decrease in the linear range. In any case, however, using QTAW the linear range (up to $500 \mu\text{g l}^{-1}$) for arsenic is considerably improved considering that obtained with QTA or MMQTA. Matousek *et al.*³³ describe an improvement in linear range using

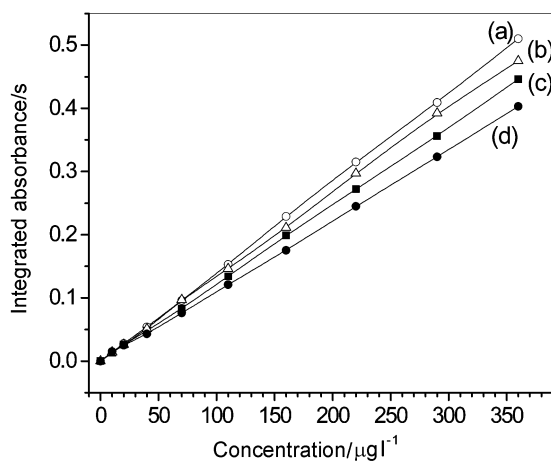


Fig. 9 Influence of different types of tungsten coil on the calibration curve for arsenic. (a) Filament A ($R^2 = 0.99986$; $Y = 0.00142 X$; $\text{LOD} = 2.1 \mu\text{g l}^{-1}$); (b) filament C ($R^2 = 0.99964$; $Y = 0.00133 X$; $\text{LOD} = 2.3 \mu\text{g l}^{-1}$); (c) filament B ($R^2 = 0.99988$; $Y = 0.00124 X$; $\text{LOD} = 2.4 \mu\text{g l}^{-1}$); (d) filament D ($R^2 = 0.99974$; $Y = 0.00111 X$; $\text{LOD} = 2.7 \mu\text{g l}^{-1}$).

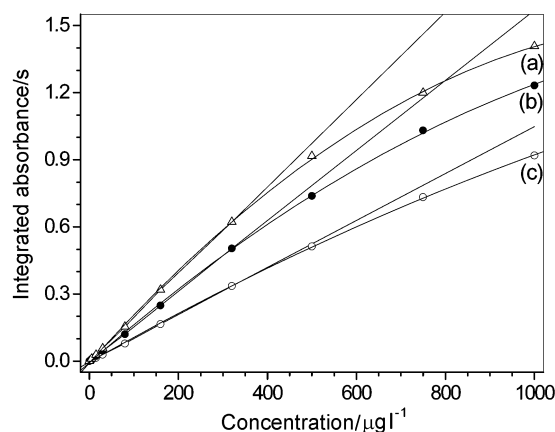


Fig. 10 Influence of reagent flow rate on the calibration curve for arsenic. (a) 6.0 ml min^{-1} flow rate ($R^2 = 0.99980$ for $0\text{--}320 \mu\text{g l}^{-1}$; $Y = 0.00195 X$; $\text{LOD} = 1.5 \mu\text{g l}^{-1}$); (b) 4.5 ml min^{-1} flow rate ($R^2 = 0.99986$ for $0\text{--}320 \mu\text{g l}^{-1}$; $Y = 0.00157 X$; $\text{LOD} = 1.9 \mu\text{g l}^{-1}$); (c) 3.0 ml min^{-1} flow rate of ($R^2 = 0.99976$ for $0\text{--}500 \mu\text{g l}^{-1}$; $Y = 0.00103 X$; $\text{LOD} = 2.9 \mu\text{g l}^{-1}$).

MMQTA (up to $100 \mu\text{g l}^{-1}$) compared with QTA. It is important to note, however, that higher flow rates, like 6.0 ml min^{-1} , may generate a large amount of water vapor that will pass through the drying gas unit. In this way, a reagent flow rate of 4.5 ml min^{-1} was considered the most appropriate for the system studied, since it allowed a good LOD ($1.5 \mu\text{g l}^{-1}$) and an analytical frequency of 60 determinations per hour.

Interferences

Dedina³¹ classified the interferences of the hydride generation technique into two groups: the liquid phase interferences and the gaseous phase interferences, while Hershey and Keliher³² stated that arsenic is one of the hydride-forming elements least susceptible to interference. In order to identify species that could interfere in the determination of arsenic using the proposed system, in liquid and gaseous phases, a study was carried out considering the constituents and the ratios between arsenic and the foreign ions present in natural and mineral water, sediment and biological materials. Solutions containing $100 \mu\text{g l}^{-1}$ of arsenic and the following amounts of the probable interferences were prepared: K (1.55 g l^{-1}); Ca (1.65 g l^{-1}); Mg (5.2 g l^{-1}); Na (43 g l^{-1}); Mn (4.4 mg l^{-1}); Zn (6.0 mg l^{-1}); Ti (6.5 mg l^{-1}); Sr (32 mg l^{-1}); Fe (60 mg l^{-1}); P (80 mg l^{-1}); Al (110 mg l^{-1}); Ag ($20 \mu\text{g l}^{-1}$); Mo ($20 \mu\text{g l}^{-1}$); Sc ($20 \mu\text{g l}^{-1}$); Sn ($20 \mu\text{g l}^{-1}$); Cd ($30 \mu\text{g l}^{-1}$); Co ($30 \mu\text{g l}^{-1}$); Se ($30 \mu\text{g l}^{-1}$); La ($60 \mu\text{g l}^{-1}$); V ($150 \mu\text{g l}^{-1}$); Ni ($300 \mu\text{g l}^{-1}$); Cr ($350 \mu\text{g l}^{-1}$); Cu ($500 \mu\text{g l}^{-1}$); Pb ($600 \mu\text{g l}^{-1}$); and Ba ($700 \mu\text{g l}^{-1}$). The interference effect was evaluated considering the difference between the absorbance for arsenic in the presence and in the absence of the element studied.

Experimental results showed that in the presence of each of the probable interference species the analytical signals correspond to 97–103% of the signal obtained for arsenic under optimized conditions, leading to the conclusion that the system was not affected by the presence of these foreign ions at the concentrations indicated and it was not necessary to add a masking reagent. Depending on the matrix, however, it is advisable to add a reagent like ascorbic acid in order to guarantee that the analyte will be present in the trivalent state.

Applications

The accuracy of the method was verified by determining arsenic in certified reference materials of sediment and biological samples. The results obtained are presented in Table 2, where the values found agree with the certified ones and the relative

Table 2 Analytical results for five certified reference materials

Sample	Certified/ $\mu\text{g g}^{-1}$	Found/ $\mu\text{g g}^{-1}$	RSD (%)
CRM 422-BCR Cod muscle	21.1 \pm 0.5	20.7 \pm 0.9	4.3
CRM 278R-BCR Mussel tissue	9.2 \pm 0.7	8.5 \pm 0.3	3.5
SRM 1566a-NIST Oyster tissue	14.0 \pm 1.2	13.2 \pm 0.4	3.0
CRM 414-BCR Plankton	6.82 \pm 0.28	6.83 \pm 0.16	2.3
CRM 320-BCR River sediment	76.7 \pm 3.4	77.0 \pm 2.0	2.6

Table 3 Analytical results for arsenic in spiked natural waters

Spike/ $\mu\text{g l}^{-1}$	Mineral water		Sea-water	
	Found/ $\mu\text{g l}^{-1}$	RSD (%)	Found/ $\mu\text{g l}^{-1}$	RSD (%)
25	24.8 \pm 1.5	6.0	25.4 \pm 1.0	3.9
50	50.8 \pm 1.0	2.0	50.8 \pm 1.6	1.6
75	75.1 \pm 1.5	2.0	76.9 \pm 1.7	1.7

standard deviations (RSD) are smaller than 5.0% for all the samples. Mineral and sea-water were also analyzed, after spiking them with known amounts of arsenic. Table 3 shows the recovery values obtained. It is possible to note that they correspond to 99–103% of the added arsenic with a RSD smaller than 6%.

Conclusions

The new quartz tube atomizer with a tungsten coil is shown to be an alternative to the conventional quartz tube atomizer, with the advantage of higher temperatures being obtained during the atomization step. The gas–liquid reactor–separator used in this study permitted using higher reagent flow rates without major problems provided the gas drying unit (DN) was well dimensioned. The use of a DN increased the lifetime of the tungsten coil without loss of sensitivity. The presence of hydrogen, generated during the formation of the hydride and swept to the atomizer, associated with the use of argon as the purge gas, allowed the required reducing environment for the adequate performance of the tungsten coil. The proposed FI-HG system, coupled to AAS with QTAW, is shown to be appropriate for generation and atomization of arsine with selectivity, good sensitivity and a low background signal. The system allowed a wide calibration range and good stability of operation along with time without losses in sensitivity. No effect of foreign species was observed. The results obtained for environmental and biological materials showed good accuracy and recovery related to the expected values.

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