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Determination of bismuth in metallurgical materials using a quartz tube atomizer with tungsten coil and flow injection-hydride-generation atomic absorption spectrometry[☆]

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Abstract

A method for the determination of bismuth in metallurgical materials using hydride generation coupled with a merging zones flow system and atomic absorption spectrometry using a quartz tube atomizer with tungsten coil is proposed. The parameters related to the bismuthine generation, the flow injection system and the use of a tungsten coil were studied and the optimized system shows a wide calibration range and good stability over time, without losses in sensitivity. The analytical curve is linear from 10 to 750 $\mu g\,l^{-1}$ of Bi with $R \geqslant 0.999$. A detection limit of 1.9 ng Bi and an analytical frequency of 60 determinations per hour were obtained. Five metallurgical reference materials were analyzed with the proposed method after their acid dissolution. The results obtained were in good agreement with certified or recommended values, and the relative standard deviations were lower than 5%.

Keywords: Bismuth determination; Quartz tube atomizer with tungsten coil; Flow injection; Hydride generation; Atomic absorption spectrometry

1. Introduction

The presence of trace amounts of bismuth may influence several characteristics of different metallurgical materials, affecting physical, mechanical and magnetic properties, depending on its concentration, and the composition of the material. In order to produce alloys of known composition, this kind of trace analyses are routine procedures for metallurgical industries [1–3].

Electrothermal atomic absorption spectrometry (ET AAS) has been largely used for trace determination of the different analytes. However, depending on the composition of the material to be analyzed, matrix separation is required for the determination of Bi by ET AAS, in order to minimize interference effects caused by concomitants, and to improve the lifetime of graphite tubes [2,4,5]. The use of the ammonium salt of dithiophosphoric acid *o,o*-diethyl ester (DDTP) has been proposed for the separation of the matrix after

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complexation and sorption onto activated carbon using a batch system [2], a manual [4] or an automated [5] flow system and, although such methods are efficient, they are not simple and can result in a low sample throughput.

Hydride generation coupled with atomic absorption spectrometry (HG AAS) has been shown to be an alternate technique with appropriate sensitivity for metallurgical materials [6]. Compared to electrothermal atomization, HG AAS is less susceptible to interferences in the atomization stage of the analyte, unless another hydride-forming element is present as a matrix element. On the other hand, severe interferences on hydride generation have been observed in the presence of several frequently used alloying elements. Thus, a species might be a severe interferent in one system, and not influence the determination of the analyte in another one. When an interference was observed in HG AAS, masking agents, such as potassium iodide [7], thiourea [1], thiosemicarbazide [8], EDTA [9] and iron [10–12], as well as higher acid or borohydride concentrations [3,10], have been successfully used.

The use of a flow injection (FI) system implies a short reaction zone that allows the separation of the generated hydride from the liquid fraction before the reduction of interferent species. This kinetic effect, coupled to the use of atomizers that provide temperatures similar to those obtained in the graphite furnace, can minimize interferences [13]. Matoušek et al. [14] proposed the use of a multiple micro-flame quartz tube atomizer (MMQTA) as an ideal hydride atomizer, but they were not able to reach temperatures higher than 1700 °C, considering the melting point of quartz.

A new quartz tube atomizer with a tungsten coil (QTAW) for the determination of gaseous species in AAS was recently developed and used for the determination of As in water, sediment and biological materials. A wide linear range, of approximately 5 times that using the MMQTA, was obtained. It was probably the first application of a flow system using a tungsten coil for the determination of arsenic following hydride generation, and the authors described the potential of the system for other hydride-forming species [15].

The objective of this work was to develop an appropriate methodology for the determination of bismuth in metallurgical materials using the QTAW and a FI-HG AAS system.

2. Experimental

2.1. Instrumentation

The generation and atomization of bismuthine was accomplished in a FI-HG system with a QTAW coupled with an atomic absorption spectrometer AAnalyst 300 (Perkin Elmer, Norwalk, CT), equipped with a deuterium lamp for background correction. The operational conditions recommended by the manufacturer were used. Integrated absorbance was used for signal evaluation, obtained by continuous graphics. The bismuth hollow cathode lamp (Perkin Elmer) was operated at 12 mA. The 222.8-nm resonance line was used with a slit-width of 0.2 nm. Argon (99.996%) from White Martins (São Paulo, SP, Brazil) was used as carrier gas for the generated hydride and for drying the Nafion® membrane in the gas-drying unit.

Four types of filaments were evaluated for QTAW: (A) 64633HLX (15 V, 150 W, Osram, Munich, Germany); (B) 64655HLX (24 V, 250 W, Osram); (C) T3Halogen (20 V, 150 W, Osram Sylvania, São Paulo, Brazil); (D) T3.15DLL (20 V, 150 W, Osram Sylvania). The temperature on the surface of the tungsten coils was measured using an Ultimax Infrared Thermometer an optical pyrometer (Ircon, Niles, IL) equipped with a Close-up VX-CL1 lens.

The metallic samples were dissolved on a hot plate from Tecnal (Piracicaba, SP, Brazil).

2.2. Samples, reagents and solutions

All chemicals used were of analytical reagent grade and water was de-ionized in a Milli-Q system from Millipore (Bedford, MA) having a resistivity of 18.2 MΩ cm. The nitric (Nuclear, São Paulo, Brazil), hydrochloric (Carlo Erba, Milan, Italy) and sulfuric acids (Merck, Darmstadt, Germany) were used for the optimization of the parameters involved in the system studied as well as for the analysis of metallurgical materials. A Nafion® 117 membrane (Aldrich: 27 467-4) was used in the gas-drying unit. The bismuth standard solution was prepared from the metal (J.T. Backer, 99.99%) treated with aqua regia under gentle heating. The final solution was diluted with 1.0 mol l^{-1} HCl. Storage was in polyethylene flasks, under cooling, and appropriate dilutions were made with 1.0 mol l^{-1} HCl from this solution, whenever necessary.

Solutions of sodium tetrahydroborate were prepared by dissolving $NaBH_4$ powder (Nuclear) in 0.5% (w/v) KOH (Nuclear) and were stored in polyethylene flasks, under refrigeration. Thiourea (Carlo Erba) and potassium iodide (Merck) were used as masking agents for the tin-based sample.

Five reference materials of metallurgical samples from the National Institute of Standards and Technology (NIST, Gaithersburg, MD, USA) were analyzed: SRM 54D (Tin-Base Bearing Metal), and 361, 362, 363 and 364 (Steels).

2.3. Sample preparation and measurement procedure

Approximately 100 mg of the tin-based sample was dissolved in 5 ml of concentrated HNO_3 under gentle heating. The filtered solution was heated with concentrated HCl, and the final solution was diluted to 100 ml in a volumetric flask with 1.0 mol l^{-1} HCl [1]. For the determination of bismuth, 5 ml of this solution was transferred to a 10-ml volumetric flask, containing 1000 mg of KI and 200 mg of thiourea. The volume was completed with de-ionized water and the solution was analyzed using the proposed system.

For the steel samples, appropriate amounts of materials (between 500 and 1000 mg) were dissolved in 20 ml of aqua regia under gentle heating, diluted to 100 ml in a volumetric flask with 1.0 mol l^{-1} HCl and filtered [3]. The solution obtained was analyzed in the proposed system for the determination of bismuth.

2.4. Flow injection system

The FI-HG system coupled to QTAW with the optimized parameters used for the determination of bismuth in metallurgical samples, as already described previously [15] is presented in Fig. 1. The major difference is an increase in the size of the gas-drying unit in order to improve the sensitivity of the system for the determination of bismuth. In this case the gas-drying unit (DN) was 6.5×5.5 cm^2, allowing the passage of gas through approximately 50 cm of membrane.

Samples, reagents and waste solution were pumped through Tygon tubes with appropriate flow rates for each solution. A known volume of sample and of reducing reagent were mixed at the confluence point and introduced into the reaction coil. A gas–liquid separator (GLS) was utilized for the separation of the generated hydride from the liquid phase. The hydride was transported with a controlled gas flow rate throughout the DN, and then introduced into the QTAW for the atomization of bismuthine.

The carriers for sample and reducing reagent were 0.5 mol l^{-1} HCl and a less concentrated (0.4% w/v) solution of $NaBH_4$, respectively, which continuously generated 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 was connected to a power supply through a copper electrode and was continuously turned on, allowing an adequate isothermal environment for the system. Under these conditions, the filament might be used for more than 130 h.

3. Results and discussion

3.1. Effect of the atomization temperature

The behavior of four different tungsten coils with different characteristics was investigated for the determination of bismuth and the result is shown in Fig. 2. For all the filaments an increase in the analytical signal was observed with increasing voltage, up to a maximum, after which it decreased. The maximum value, independent of the bismuth concentration, was reached with 4.0 V for filament A, with 5.0 V for filaments B and C, and with 5.5 V for filament D.

The temperature at the coil surface of the different filaments was measured with an optical

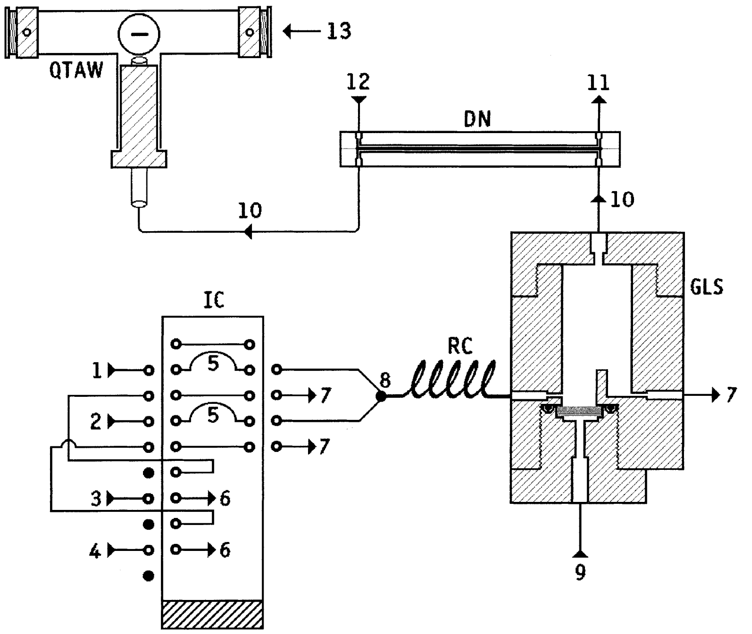

Fig. 1. Flow diagram of the proposed system. IC: injector–commutator; RC: reaction coil (30 cm long, 0.8 mm i.d.); GLS: gas–liquid separator; DN: gas-drying unit with Nafion® membrane; QTAW: quartz tube atomizer with tungsten coil (Filament A: 4.0 V); (1) 0.5 mol l^{-1} HCl (4.5 ml min^{-1}); (2) 0.4% w/v $NaBH_4$ in 0.5% w/v KOH (4.5 ml min^{-1}); (3) sample; (4) 0.8% w/v $NaBH_4$ in 1.0% w/v KOH; (5) injection volume (500 μl); (6) recirculation; (7) waste; (8) confluence point; (9) Ar (450 ml min^{-1}); (10) gas flow; (11) humid gas; (12) Ar (600 ml min^{-1}); (13) radiation beam of AAS.

pyrometer, for the different applied voltages, and the most adequate signals for bismuth determination were obtained with a temperature of approximately 1460 ± 70 °C. This is higher than the values obtained with quartz tube atomizers with electric or flame heating. Despite the lack of information about the mechanism of atomization for this kind of system, the results obtained suggest that the atomization of bismuthine occurs preferentially in the areas close to the gaseous phase and not at the surface of the filament. On the other hand, the geometry of the filament may also influence the atmosphere inside the QTAW, especially the transfer of heat. Similar behavior was also obtained for arsenic [15].

3.2. Effect of acid concentration

Identical concentrations of hydrochloric acid are recommended for the dilution of the sample solution containing bismuth and as its carrier [1]. The

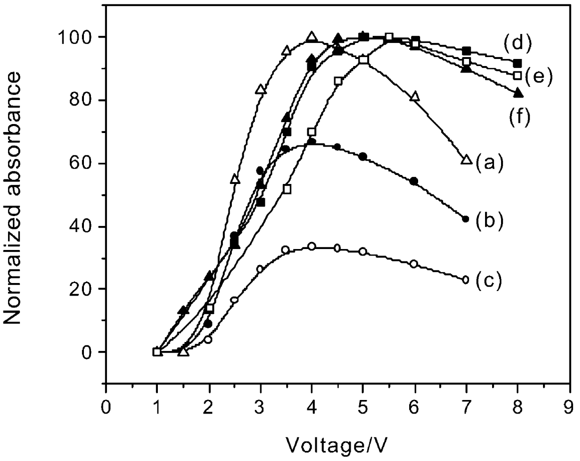

Fig. 2. Effect of the voltage applied to the tungsten coil on the sensitivity for bismuth. (a) Filament A and 250 μg l^{-1} Bi; (b) filament A and 160 μg l^{-1} Bi; (c) filament A and 70 μg l^{-1} Bi; (d) filament C and 250 μg l^{-1} Bi; (e) filament D and 250 μg l^{-1} Bi; (f) filament B and 250 μg l^{-1} Bi.

effect of hydrochloric acid concentration on the efficiency of hydride generation, considering different concentrations of bismuth as well as the effect of different acids (mainly those generally used for the sample treatment) was evaluated. The experimental results showed that increasing the concentration of HCl the signal for different bismuth concentrations was not affected above 1.0 mol l^{-1}. The presence of other acids, such as HNO_3, $HClO_4$ and H_2SO_4, which are commonly used in the sample treatment step, and that are sometimes not completely removed from the final solution, affects the determination of bismuth. These results are in agreement with those obtained previously [1]. When sample treatment is required it is advisable to use a minimum volume of these acids in order to avoid interference effects.

3.3. Effect of sodium tetrahydroborate concentration

The effect of the $NaBH_4$ concentration was studied in the range of 0.5–2.5% w/v, and the results show that the determination of bismuth was not severely affected when the concentration of the reducing agent increased. A concentration of 0.7% w/v of $NaBH_4$ was selected as appropriate considering the absorbance and the repeatability obtained for different concentrations of bismuth. While lower concentrations might not be enough for the complete conversion of bismuth to the hydride, higher concentrations will generate an excess of hydrogen and an excess of water vapor that might cause damage to the filament.

3.4. Effect of reaction coil and injection volume

The length of the reaction coil, where the analyte, the HCl and the $NaBH_4$ are in contact, determines the reaction time necessary to guarantee the conversion of bismuth to bismuthine. Different lengths of reaction coils were evaluated, and the result showed that the formation of bismuthine is practically independent of the reaction time, and might occur immediately after the reagents get into contact. A reaction coil of 30 cm was chosen as being appropriate considering sensitivity and repeatability. Fig. 3(1) shows the effect of the injected sample and reducing agent volume on the determination of bismuth. An increase in the injection volume implies an increase in the analytical signal and this result was the same for different concentrations of bismuth. Although adequate analytical signals were obtained with small injection volumes, the sensitivity was improved with higher volumes, as can be seen in Fig. 3(2). Taking this into account, however, special care with the efficiency of the hydride separation from the liquid phase must be taken. Injection volumes of 500 μl were selected for the studied system.

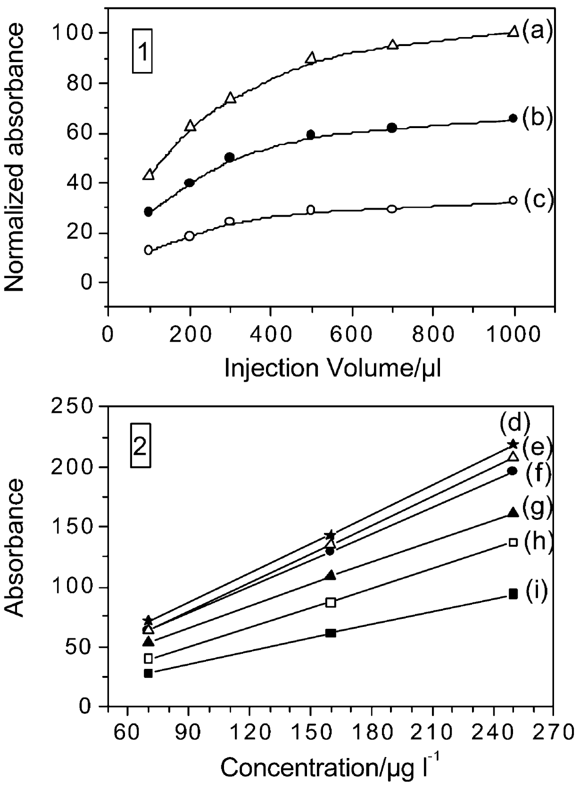

Fig. 3. Effect of the injected volume of the sample and reducing agent: (1) On the sensitivity of bismuth using different concentration. (a) 250 μg l^{-1}; (b) 160 μg l^{-1}; (c) 70 μg l^{-1}. (2) On the inclination of the analytical curve. (d) 1000 μl; (e) 700 μl; (f) 500 μl; (g) 300 μl; (h) 200 μl; (i) 100 μl.

3.5. Effect of carrier gas flow rate

The carrier gas flow rate may significantly influence the determination of bismuth, as can be

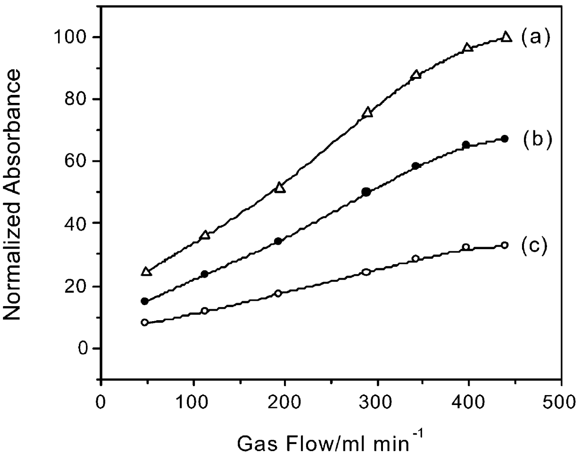

Fig. 4. Effect of Ar carrier gas flow rate on the efficiency of hydride generation. (a) 250 μg l^{-1}; (b) 160 μg l^{-1}; (c) 70 μg l^{-1}.

observed in Fig. 4. As has been reported previously, bismuth hydride is very unstable and may decompose even at ambient temperature [16]. Hence, the hydride must be quickly transported to the atomizer, using a high carrier gas flow rate. Under this condition the generated BiH_3 may be diluted but, in this study, it was observed that argon flow rates of 400–450 ml min^{-1} gave the best analytical signals.

3.6. Effect of reagents flow rate

The reagent flow rate may influence the determination of bismuth using the FI-HG with QTAW system. Thus, the effects of carrier flow rates (HCl and $NaBH_4$) in the FI system on the bismuth signal were determined. The absorbance was measured when the flow rates of reagents were 3.0, 4.5 and 6.0 ml min^{-1} for increasing bismuth concentrations, up to 1200 μg l^{-1}. As can be seen in Fig. 5, an increase in the reagent flow rate leads to a larger inclination of the analytical curve and a consequent improvement in LOD. It is important to note, however, that higher flow rates, such as 6.0 ml min^{-1}, might generates a large amount of water vapor that might pass through the gas-drying unit. A reagent flow rate of 4.5 ml min^{-1} was considered most appropriate for the system studied, since it allowed good LOD and a sampling frequency of up to 60 determinations per hour.

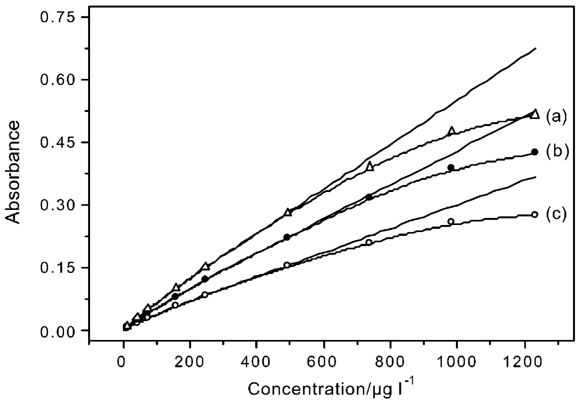

Fig. 5. Effect of reagent flow rate on the analytical curve for bismuth. (a) 6.0 ml min^{-1} ($R=0.9992$ for 0–500 μg l^{-1}; $Y=0.000564X$; LOD = 5.3 μg l^{-1}); (b) 4.5 ml min^{-1} ($R=0.9990$ for 0–750 μg l^{-1}; $Y=0.000426X$; LOD = 7.0 μg l^{-1}); (c) 3.0 ml min^{-1} ($R=0.9991$ for 0–500 μg l^{-1}; $Y=0.000308X$; LOD = 9.7 μg l^{-1}).

3.7. Effect of different tungsten coils on the analytical curve

The effect of different designs of tungsten coils on the atomization of bismuth in the QTAW was

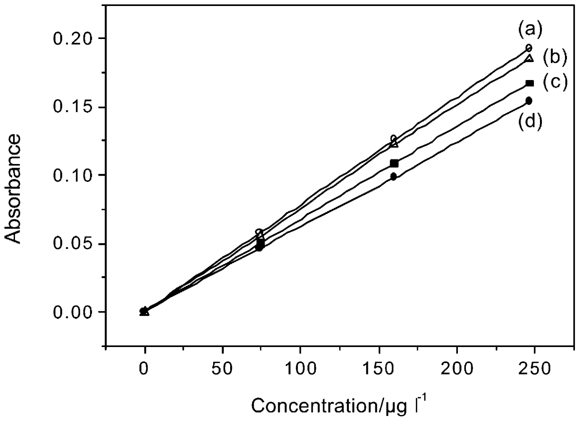

Fig. 6. Effect of different designs of tungsten coils on the analytical curve for bismuth. (a) Filament A ($R=1$; $Y=0.000784X$; LOD = 3.8 μg l^{-1}); (b) Filament C ($R=0.99985$; $Y=0.000755X$; LOD = 4.0 μg l^{-1}); (c) Filament B ($R=0.99999$; $Y=0.000679X$; LOD = 4.4 μg l^{-1}); (d) Filament D ($R=0.99984$; $Y=0.000622X$; LOD = 4.8 μg l^{-1}).

Table 1
Figures of merit for the determination of bismuth in metallurgical materials after acid digestion

Analytical range ($\mu g\, l^{-1}$)	LOD (ng)	R.S.D. (%)	*R*	Sampling frequency (h^{-1})
10–750	1.9	<5	0.9999	60

investigated. Analytical curves for the different filaments were established, using the optimized parameters and concentrations of bismuth up to 1200 $\mu g\, l^{-1}$. The best value of applied voltage for each filament was used. The results of this study are presented in Fig. 6, and it may be observed that all the filaments showed good responses relative to the linear range, with small changes in sensitivity. This study allowed concluding that QTAW is not dependent of the geometry of tungsten coil for the determination of bismuth. The small changes in sensitivity observed certainly originate from the internal environment of the atomizer, which depends on the differences in heat transfer caused by the type of filament coil. In conclusion, it was observed that any of the evaluated coils might be used with success in QTAW.

3.8. Analytical figures of merit and applications

Table 1 summarizes the analytical figures of merit for the determination of bismuth. The accuracy of the method was verified by determining bismuth in five reference materials of metallurgical samples after their acid dissolution. The results obtained are presented in Table 2, and the values found are in agreement with the certified or recommended one's and the relative standard deviations (R.S.D.) are smaller than 5.0% for all the samples. Although the concentrations of samples 363 and 364 were not in best agreement with the recommended values, they are close to the results obtained by other authors [2,3].

In the case of the tin-based alloy, the addition of KI and ascorbic acid was necessary, in order to overcome the interference effects. The formation of precipitates during the treatment was not observed. The determination of bismuth in the steel samples was adequate, leading to the conclusion that the determination was not affected by the presence of other species, i.e. there was no need of using a masking reagent. The high temperature of the QTAW, associated with the use of an FI system, resulted in an overall low interference effect.

Table 2
Determination of bismuth in different reference materials using the QTAW system coupled to FI-HG AAS

Sample	Theoretical (%)	Found (%)	R.S.D. (%)
54D	0.044 ± 0.005^{a}	0.044 ± 0.001	2.3
361	$(0.0004)^{b}$	0.00044 ± 0.00002	4.5
362	$(0.002)^{b}$	0.00233 ± 0.00003	1.3
363	$(0.0008)^{b}$	0.00060 ± 0.00002	3.3
364	$(0.0009)^{b}$	0.00131 ± 0.00002	1.5

[a] Certified value.

[b] Recommended values.

4. Conclusions

The FI-HG system studied, coupled to AAS with QTAW, was demonstrated to be appropriate for generation and atomization of bismuthine, with selectivity, good sensitivity and low background signal. The system allowed a wide analytical range and good stability of operation over time without losses in sensitivity. The results obtained for metallurgical materials showed good accuracy and recovery of the expected values. The potentiality of this system leads to the conclusion that bismuth can also be determined in other kinds of samples.

Acknowledgments

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