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Analytical Note

In situ atom trapping of Bi on W-coated slotted quartz tube flame atomic absorption spectrometry and interference studies

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ABSTRACT

Analytical performances of metal coated slotted quartz tube flame atomic absorption spectrometry (SQT-FAAS) and slotted quartz tube in situ atom trapping flame atomic absorption spectrometry (SQT-AT-FAAS) systems were evaluated for determination of Bi. Non-volatile elements such as Mo, Zr, W and Ta were tried as coating materials. It was observed that W-coated SQT gave the best sensitivity for the determination of Bi for SQT-FAAS and SQT-AT-FAAS. The parameters for W-coated SQT-FAAS and W-coated SQT-AT-FAAS were optimized. Sensitivity of FAAS for Bi was improved as 4.0 fold by W-coated SQT-FAAS while 613 fold enhancement in sensitivity was achieved by W-coated SQT-AT-FAAS using 5.0 min trapping with respect to conventional FAAS. MIBK was selected as organic solvent for the re-atomization of Bi from the trapping surface. Limit of detection values for W-coated SQT-FAAS and W-coated SQT-AT-FAAS was obtained as 0.14 μg mL^{-1} and 0.51 ng mL^{-1}, respectively. Linear calibration plot was obtained in the range of 2.5–25.0 ng mL^{-1} for W-coated SQT-AT-FAAS. Accuracy of the W-coated SQT-AT-FAAS system was checked by analyzing a standard reference material, NIST 1643e.

1. Introduction

Atomic spectrometric methods such as flame atomic absorption spectrometry (FAAS) [1], atomic fluorescence spectrometry (AFS) [2], electrothermal atomic absorption spectrometry (ETAAS) [3], inductively coupled plasma optical emission spectrometry (ICP-OES) [4] and inductively coupled plasma mass spectrometry (ICP-MS) [5] have been used for determination of Bi in a variety of samples; some approaches in solid environmental samples have been reviewed [6]. Sensitivity of FAAS method is not sufficient for determination of Bi in many real samples. Hence, an analytical step such as preconcentration, hydride generation or extraction is needed before FAAS detection [6,7]. There are two major factors limiting the sensitivity of FAAS. The first one is about the low efficiency of the conventional nebulization process. Only a small portion of sample, 1–10%, can be transported to atomizer. The second drawback of FAAS is the short residence time of analyte in the measurement zone, limiting interactions of analyte atoms with monochromatic source light and thus lowering the sensitivity [7–10]. For alleviation of this problem, researchers have focused on several sensitivity enhancement methods. Delves' microsampling cup [11], slotted quartz tube (SQT) [12], chemical vapor generation [13] and electrothermal atomizers for AAS [14] are some of the methods used in the literature to improve sensitivity for various elements. In situ preconcentration techniques for flame atomic absorption spectrometry have been reviewed by Matusiewicz [7].

SQT-FAAS recommended by Watling for the first time was used for on-line sensitivity enhancements for Pb, Cd and Cu [12]. Variations of analytical signals as a function of internal diameter, the length of the upper slot and the wall thickness of quartz tube were investigated [15]. SQT was also applied for determination of Pb, Cd and Cu in environmental samples [16], Pb and Cd in plant leaves [17], and Pb and Cd in cancerous (malign) and noncancerous (adenoma) human thyroid tissues [9].

Atom trapping is another effective method to improve the sensitivity of FAAS. One kind of atom trapping is based on the collection of analyte atoms on inner surface of SQT for a proper time period and revolatilization of trapped atoms to obtain the analyte signal by using a small volume of organic solvent, such as methyl isobutyl ketone [8]. This method is named as slotted quartz tube-atom trapping-flame atomic absorption spectrometry (SQT-AT-FAAS). The method was introduced in 2002 [18,19] and has been reviewed [8]. Recent applications involve determinations of indium [20], Bi [21], and Sb [22]. The advantages of slotted quartz tube-atom trap (SQT-AT) were highlighted by Ataman as high sensitivity, lower interference possibility, high sample throughput, low cost and simplicity [8,10].

SQT can be coated with different metals to improve sensitivity. Brown and Milner coated SQT with Al and La solutions to prevent the tube from devitrification [23]. It is important that melting point of the

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coating material should be higher than that of the analyte. This approach was investigated and tested to improve the sensitivity of SQT-AT-FAAS; for this purpose, non-volatile elements such as Ta, Zr, Mo, Ti or Au were selected as coating materials in view of their higher melting and boiling points [22]. For determination of Sb by SQT-AT-FAAS, the coating process did not provide a significant improvement and thus was not used [22].

In our previous study, slotted quartz tube-atom trap-flame atomic absorption spectrometry (SQT-AT-FAAS) technique was employed for the sensitivity improvement of FAAS for Bi [21]. It was highlighted that the proposed technique could be suitable for most water sample analyses. In this study, further improvement in sensitivity was obtained for Bi determination at ultra-trace levels by using metal coated SQT-AT-FAAS. Non-volatile metals were used for coating of inner surface of SQT. All of the system parameters were optimized. Interference studies were also performed and presented.

2. Experimental

2.1. Reagents and materials

All the reagents were of analytical grade unless stated otherwise. Glassware and plastic containers were kept in 1.0 mol L^{-1} HNO_3 overnight and rinsed with distilled water prior to use. Bismuth standard solution, 1000 ± 3.0 mg L^{-1}, was supplied from High Purity Standards-Charleston, SC, USA. HCl, H_2O_2 and NaOH were supplied from Sigma-Aldrich (St. Louis, USA). For the interference studies, Na, Mg, K, Fe, Co, Ni, Cu, Cd, Se, Sb, Zn, Sn and Al solutions were prepared from their 1000 mg L^{-1} stock solutions. SO_4^{2-}, Cl^- and NO_2^- solutions were prepared from Na_2SO_4, NaCl and $NaNO_2$ in water, respectively. Standard reference material, namely Trace Elements in Water-SRM 1643e, was supplied from NIST (Gaithersburg, MD, USA). For the coating of SQT, Ta, Zr, W, and Mo solutions were used. Mo and W solutions were prepared from their 1000 mg L^{-1} standard solutions (Ultra Scientific Standards, Rhode Island, USA). For Ta solution, Ta_2O_5 was dissolved in 3.0 mol L^{-1} HF. In order to prepare Zr solution, $Zr(NO_3)_4 \cdot 5H_2O$ was dissolved in 1.0 mol L^{-1} HNO_3.

2.2. Sampling

Concentrations of Bi in two tap water samples and a river water sample from Tigris River in Diyarbakır-Turkey were determined by W-coated SQT-AT-FAAS system. Two tap water samples from Diyarbakır and Elazığ cities in Turkey were collected and kept in glass bottles. The container was flushed with sampled water for 5.0 min before sampling. Samples were filtered through 0.45 μm membrane filter to remove particles and then acidified with 0.50 mL of HNO_3 to prevent precipitation. Two different brands of natural spring water were bought from local market of Diyarbakır. An amount of 1000 mL portion of each sample was transferred to a beaker. Dissolved gases in samples were removed by using an ultrasonic bath for 10.0 min. For the river sample, a total of 5.0 L sample water was collected from different locations of Tigris River and then mixed. Sample was acidified by 2.5 mL of concentrated HNO_3, transported to the laboratory and filtered through 0.45 μm membrane filter. All the samples were analyzed on the same day of sample collection. External calibration method was applied in all of the measurements.

2.3. Instrumentation and apparatus

An ATI UNICAM model 929 flame atomic absorption spectrometer (Cambridge, UK) was used with a 10 cm air-acetylene burner head. Signals were processed with Solaar software on Windows 98. A Cathodeon (Cambridge, UK) Bismuth hollow cathode lamp was used as a radiation source with an operating current of 9.0 mA. Deuterium (D_2) background correction was used throughout this study. All the measurements were performed at the wavelength of 223.1 nm and a spectral band pass of 0.5 nm.

A 14 cm long slotted quartz tube with two slots positioned at 180° with respect to each other was used; lengths of the lower and the upper slots were 100 mm and 40 mm, respectively. Inner diameter of the tube was 10 mm and the outer diameter was 12 mm. The slotted quartz tubes were prepared by Çalışkan Cam, Ankara, Turkey. During the coating process, SQT was positioned on top of burner head and 100 mL of 100 mg L^{-1} solutions of Ta, Zr, W or Mo was aspirated with a suction rate of 4.0 mL min^{-1} into a lean flame.

In SQT-AT-FAAS, 20.0 ng mL^{-1} of Bi solution was aspirated to flame for trapping of analyte on inner surface of the metal coated SQT using a lean flame for 2.0 min. 50 μL of MIBK was used by using conventional nebulization for the revolatilization of Bi from SQT surface following the collection cycle. Then, transient signals were recorded and their peak height was used in analysis.

Vibrational spectroscopy measurements were performed by using Jobin-Yvon LabRam Raman Confocal Microscope (Palaiseau, France); the Raman spectrometer had a charge-coupled device detector and a holographic notch filter. In the preparation of samples for Raman spectrometric studies, no SQT's were sacrificed. Instead, 1.0 × 1.0 cm planar quartz pieces were placed in SQT; following the coating procedure applied the quartz pieces were removed and subjected to spectrometric analysis. Both bare and W-coated quartz surfaces for Raman spectrometry were loaded by analyte by aspirating 100 mL of 1000 mg/L Bi solution into a lean air/acetylene flame while the SQT was mounted as usual.

3. Results and discussion

3.1. Optimization studies

All of the parameters were optimized to obtain the best S/N ratio. In the optimizations, the tested parameter was varied while the others were kept constant at or near their optimum values.

3.1.1. Optimization of metal coated SQT-FAAS system

Melting point of the coating material is an important parameter. It should be higher than the melting point of analyte. Coating material should not be significantly lost from the surface while element is revolatilized from the SQT surface. For this purpose, Mo, Zr, W and Ta were selected and tested as coating metals. Sensitivities of Mo, Zr and Ta coated SQT-FAAS systems were lower than the W-coated SQT-FAAS system, the lowest sensitivity was obtained from the uncoated SQT (Table 1). The highest sensitivity was obtained by using W as the coating metal. Furthermore, the highest signal to noise ratio was found also in the case of W-coated SQT-AT-FAAS for Bi. The melting point of W is higher than the other metals tested for coating; in addition the conditions for the trapping and revolatilization of analyte from this surface must have been more favorable. The experimental evidence has shown that W as a coating metal proved to be a more suitable surface as compared with Mo, Zr or Ta for both SQT-FAAS and SQT-AT-FAAS. For W-coated SQT-FAAS, the response given for 10.0 μg mL^{-1} Bi in Table 1 as 0.194 ± 0.012 absorbance is significantly higher than

Table 1
Effect of coating material on 10.0 μg mL^{-1} Bi signal for metal coated SQT-FAAS method ($n = 3$). Softening point for quartz is 1665 °C.

Coating metal	Melting point, °C	Mean absorbance ± SD[a]	RSD[b], %
None	–	0.150 ± 0.010	6.7
Mo	2623	0.167 ± 0.014	8.4
Zr	1855	0.176 ± 0.013	7.4
W	3422	0.194 ± 0.012	6.2
Ta	3017	0.185 ± 0.013	7.0

[a] SD, standard deviation.

[b] RSD, relative standard deviation.

the value given for no coating, 0.150 ± 0.010 absorbance, at both 95% and 99% confidence levels using Student's *t*-test.

Effects of acetylene flow rate, sample suction rate and height of SQT from burner head for W-coated SQT-FAAS were investigated in the ranges of 0.6–2.0 L min^{-1}, 3.4–5.6 mL min^{-1} and 2.0–5.0 mm, respectively. Optimum conditions are given in Table 2. Analytical features of W-coated SQT-FAAS are summarized in Table 3. RSD was calculated as 7.0% for seven replicate measurement of 0.5 mg L^{-1} Bi.

3.1.2. Optimization of W-coated SQT-AT-FAAS system

W-coated SQT was used in the further studies because W was selected as the best coating material among the tested coating metals to improve the sensitivity of Bi determination by SQT-AT-FAAS system. All of the experimental variables such as the type and volume of organic solvent, fuel type, suction rate of sample, height of SQT and trapping period were optimized.

Raman spectroscopy was employed to investigate the coating of W on SQT and Bi species trapped on W-coated SQT. Raman spectra of bare quartz, Bi species trapped on quartz, W-coated quartz and Bi species trapped on W-coated quartz are given in Fig. 1. It is clear that similar spectra were observed in case of Bi coating on quartz and Bi coating on W-coated quartz (Fig. 1b, d). Individual double peaks at 1000 cm^{-1}, triple peaks at 520 cm^{-1} and the sharp peak at 250 cm^{-1} with a small peak at 170 cm^{-1} prove that Bi species are trapped on SQT and W-coated SQT with the same chemical structure.

Highly flammable organic solvents such as ethyl alcohol, methyl alcohol, acetonitrile, 2-propanol, tetrahydrofurane (THF), methyl ethyl ketone (MEK) and methyl isobutyl ketone (MIBK) were tried for the revolatilization of Bi on W-coated SQT surface. Type of organic solvent is very important for the rapid revolatilization of Bi species from the SQT surface. Among the tested chemicals, the highest sensitivity was obtained with MIBK. Ethyl alcohol, methyl alcohol and acetonitrile gave the similar Bi signals. In the case of THF, it was observed that flame was not stable and was extending over the SQT through the upper slot. MIBK was selected as the best organic solvent for further studies in W-coated SQT-AT-FAAS. In our previous work, MEK had been selected as the organic solvent for revolatilization of Bi from uncoated SQT surface [21]. W has a higher melting point of 3422 °C as compared with the other coating metals tested in this study and W-coated SQT has a high efficiency for Bi trapping. However, Bi was not efficiently revolatilized from the W-coated quartz surface by MEK while the experiments with MIBK gave better results. It could be attributed to the ratio of carbon/oxygen of organic solvents that contribute to revolatilization and/or reatomization of Bi on coated surface. MIBK ($C_6H_{12}O$) presents a higher C/O ratio than MEK (C_4H_8O). Therefore, when the organic solvent is introduced, in the momentarily formed fuel rich acetylene/air flame the C/O ratio may be an important factor for the W-coated SQT surface. However, at this point this is only an empirical result since the effect of C/O ratio did work just the opposite way in the case of SQT-AT-FAAS where MEK was the preferred solvent [21].

After the selection of MIBK as the organic solvent for the revolatilization of Bi from W-coated SQT surface, its volume was also optimized to obtain the highest sensitivity. MIBK volume was varied in the range of 20–70 μL. It was observed that Bi signal reached to the highest value when 50 μL of MIBK was used. Lower signals obtained for the volumes less than 50 μL were attributed to insufficient revolatilization; for the higher volumes the change in the composition of the flame gases was noticeable and thus using volumes of MIBK higher than 50 μL was not necessary or desirable.

Using a constant trapping period of 2.0 min and MIBK for revolatilization and a constant acetylene flow rate of 0.6 L min^{-1}, analytical parameters were varied to find the optimum values. The optimum conditions for W-coated SQT-AT-FAAS are given in Table 2. For the volume of organic solvent, the optimum value of 50 μL was found after trying values in the range of 20–70 μL. Sample suction rate and height of SQT were tested in the ranges of 4.0–5.5 mL min^{-1} and 2.0–5.0 mm, respectively. Trapping period was investigated in the range of 1.0–5.0 min. Optimum conditions are summarized in Table 2.

Table 2
Optimum experimental conditions for W-coated SQT-FAAS and W-coated SQT-AT-FAAS method.

Parameter	W-coated SQT-FAAS	W-coated SQT-AT-FAAS
Type of organic solvent	–	MIBK
Volume of organic solvent, μL	–	50
Flow rate of acetylene, L min^{-1}	0.6	0.6
Sample suction rate, mL min^{-1}	5.6	5.5
Height of SQT, mm	2.0	2.0
Trapping period, min	–	5.0

3.2. Analytical figures of merit

Analytical figures of merit for W-coated SQT-FAAS are given in Table 3, using the optimum values given in Table 2 and a trapping period of 5.0 min. RSD value was calculated as 7.2% for seven replicate measurements of 2.5 ng mL^{-1} Bi. Signal for 20.0 ng mL^{-1} of Bi solution by W-coated SQT-AT-FAAS can be seen in Fig. 2. The half bandwidth of this transient signal was found to be 0.5 s.

In this study, sensitivity enhancement for W-coated SQT-FAAS and W-coated SQT-AT-FAAS was calculated by comparing the C_0 values. Enhancement factors in terms of unit time, E_t, and unit volume, E_v, have been introduced by Ataman [8]. Other analytical parameters in Table 3 were described in our previous study [21]. Hence, using these values as enhancement factors, sensitivities can be compared in terms of the trapping period and the total sample volume used; E, E_t and E_v values for W-coated SQT-FAAS and W-coated SQT-AT-FAAS systems are shown in Table 3 with respect to FAAS for Bi determination.

In our previous report the applicability of the SQT-AT-FAAS technique for the in situ preconcentration of Bi on uncoated slotted quartz tube was demonstrated [21]. Sensitivity was improved by 256 times by SQT-AT-FAAS with respect to conventional FAAS. LOD for a collection time of 6.0 min (36.0 mL of solution) was reported as 1.6 ng mL^{-1} [21]. Further improvements in sensitivity were achieved by coating the inner surface of SQT using a W solution. Sensitivity of conventional FAAS was improved as 613 times using W-coated SQT-AT-FAAS. Enhancement in sensitivity was improved by a factor of 2.4 by W-coated SQT-AT-FAAS with respect to SQT-AT-FAAS without any metal coating. The improvement in sensitivity could be attributed to the better trapping and revolatilization conditions achieved with a W-coated SQT surface. Further improvement in sensitivity as 1.4 fold was also achieved in SQT-FAAS when SQT was coated with W. With a simple modification, important enhancement in sensitivity was achieved. In this study, LOD and LOQ were found to be 0.51 and 1.7 ng mL^{-1}, respectively for W-coated SQT-AT-FAAS. It should be noted that prolonged use of W-coated SQT for trapping of Bi affected the efficiency of the tube. A freshly coated tube could be used for as much as 50 cycles with samples of simple matrices, while for samples containing alkali metals in concentrations as high as 2000 ng mL^{-1}, sensitivity may decrease after even 3–4 cycles. In this case, recoating of the tube was required after immersing SQT into 5% (v/v) HF for a few minutes.

Several techniques used for determination of technique, along with the present study are given in Table 4, including the detection limits. The sensitivity of the method proposed in this study is compatible with the methods used in the literature. W-coated SQT-AT-FAAS can be an alternative detection method for the detection of bismuth in laboratories where sensitive instruments such as ICP-OES and ICP-MS are not available.

3.3. Interference studies on W-coated SQT-AT-FAAS

Interference studies were performed in order to investigate the possible effect of some species on bismuth determination by W-coated

Table 3
Analytical figures of merit for W-coated SQT-FAAS and W-coated SQT-AT-FAAS systems.

Method	Linear range	Slope	Intercept	R^2	LOD	LOQ	C_0	m_o, ng	E^{e}	E_t^{f} min^{-1}	E_v^{g} mL^{-1}
FAAS^{a}	2.0–50.0^{b}	0.0045	0.0128	0.9986	0.47^{b}	1.57^{b}	0.87^{b}	–	1.0	–	–
W-coated SQT-FAAS	0.5–20.0^{b}	0.0192	0.0044	0.9966	0.14^{b}	0.46^{b}	0.22^{b}	–	4.0	–	–
W-coated SQT-AT-FAAS^{d}	2.5–25.0^{c}	0.0031	0.0017	0.9991	0.51^{c}	1.7^{c}	1.4^{c}	39	613	123	22
SQT-FAAS^{h}	0.5–20.0^{b}	0.0134	0.0106	0.9981	0.11^{b}	0.37^{b}	0.30^{b}	–	2.9^{h}	–	–
SQT-AT-FAAS^{h}	7.5–100^{c}	0.0010	0.0063	0.9919	1.60^{c}	5.30^{c}	3.4^{c}	122	256^{h}	43	7.1

[a] Experimental conditions; flow rate of air: 4.0 L min^{-1}, flow rate of acetylene: 1.5 L min^{-1}, sample suction rate: 8.5 mL min^{-1}.
[b] μg mL^{-1}.
[c] ng mL^{-1}.
[d] Sample suction rate: 5.5 mL min^{-1}, trapping period: 5.0 min for W-coated SQT-AT-FAAS.
[e] E is enhancement, C_0(FAAS) / C_0 (related method).
[f] $E_t = E$ / t.
[g] $E_v = E$ / v.
[h] From Ref. [21].

SQT-AT-FAAS. The analyte concentration was kept constant as the analytical signal was monitored for the interferent/analyte (w/w) ratios of 1, 10 and 100. The analyte concentration was 20 ng mL^{-1} Bi, while in the similar study 75 ng mL^{-1} Bi was used for SQT-AT-FAAS [21]. The uncertainty for the values obtained varied between 5 and 7% while the similar values observed for SQT-AT-FAAS system were in a range of 5–8% [21]. For the following paragraphs, the mentioned and defined ratios of 1, 10 and 100 will be used. Any difference which is equal to or less than 8% will be considered as not significant. Any comments regarding a comparison with SQT-AT-FAAS system, the values are taken from the previous study [21]. The absence of a comment for any interferent and ratio notes there is no significant effect.

For W-coated-SQT-AT-FAAS, Na has no significant effect at the ratios of 1 and 10, while a 17% suppression is observed for the ratio of 100; for the same ratio, suppression was 26% for SQT-AT-FAAS. Using SQT-AT-FAAS, Ca causes an enhancement of 9% at ratio of 1; 10% suppression is observed at ratio of 100; at the same ratio, the effect is 13% suppression for SQT-AT-FAAS. Mg and Mn have no significant effect at all the ratios tested using W-coated-SQT-AT-FAAS, while Mg causes suppression by 14% at the ratio of 100 in case of -SQT-AT-FAAS. Fe has no effect in both techniques but Zn causes suppression by 12% at the ratio of 100 for SQT-AT-FAAS. Al causes an enhancement by 9% at the ratio of 1 but suppression by 19% at the ratio of 100 in W-coated-SQT-AT-FAAS; the effects are not significant for SQT-AT-FAAS. For W-coated-SQT-AT-FAAS, at the ratio of 100, Co and Cu have suppression effects by 10% and 14%, respectively; Cu has a suppressing effect by 10% also at the ratio of 10. The effects of Co and Cu are not significant in SQT-AT-FAAS. Nickel has suppression effect by 9% and 12% at the ratios of 1 and 100, respectively for W-coated-SQT-AT-FAAS; the effect is not significant in case of SQT-AT-FAAS. Mo and Sn have no effect at all the interferent/analyte (w/w) ratios in both techniques. On the other hand, Mn, Cr, Fe, Zn, Al, Co, Cu, Ni, Mo, Sn and Se have no significant effect at all the ratios in the case of SQT-AT-FAAS. A decrease of signal by 14% was observed for Sb, when the ratio was 100 in W-coated-SQT-AT-FAAS. For SQT-AT-FAAS at the ratio of 10, Sb caused suppression by 10%. Sulfate ion caused an enhancement by 10% at the ratio of 1 while 10% and 17% suppression were observed at the ratios of 10 and 100, respectively; for SQT-AT-FAAS, suppression was 12% at the ratio of 100. Chloride had a suppression effect by 10% at the ratio of 100; the same value for the same case was obtained for SQT-AT-FAAS.

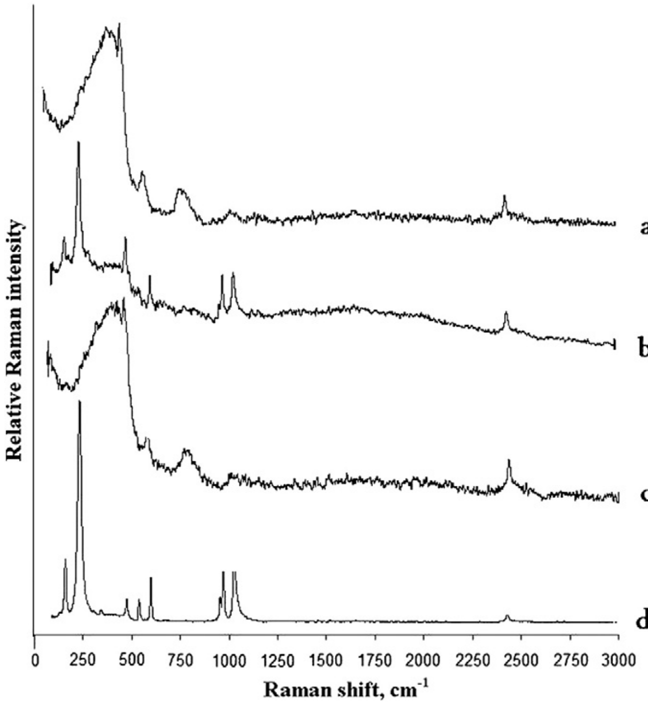

Fig. 1. Comparison of Raman spectra of a) quartz, b) Bi trapped on quartz, c) W-coated quartz, d) Bi trapped on W-coated quartz.

For W-coated-SQT-AT-FAAS, the cases of Cr and Se are rather unexpected. At the ratios of 1 and 10, suppression effect by 14% and 10% were observed for Cr while there was no significant effect at the ratio of 100. Similarly, for the Se the suppression values are 15%, 5% and 10% for the ratios of 1, 10 and 100, respectively. The observed interference effect of Cr and Se is higher at lower interferent concentrations. Although the reason for these phenomena cannot be explained at this moment, similar behavior was also observed during the determination of indium by SQT-AT-FAAS; almost 10% decrease was observed at the ratio of 1 while enhancement was observed at higher interferent concentrations [20].

In general, interference effects observed on Bi by the interferents used in this study are not excessively high indicating that the use of external calibration may be used in many cases. The comparison between the W-coated-SQT-AT-FAAS and SQT-AT-FAAS must be made noting the different analyte concentrations used, namely 20 ng mL^{-1} and 75 ng mL^{-1} Bi, respectively.

During the interference studies, extended use of W-coated SQT resulted in the reduction of sensitivity. The response was frequently tested by trapping and revolatilizing 20.0 ng mL^{-1} of Bi; when the reduction in signal was higher than 8% the response was restored by keeping SQT in 5% HF for a few minutes and rinsing with water. The interference study was continued after the sensitivity was at the desired level.

3.4. Accuracy check and application of W-coated SQT-AT-FAAS system

SRM, NIST 1643e, trace elements in water, was used to check the accuracy of W-coated SQT-AT-FAAS system. External calibration method

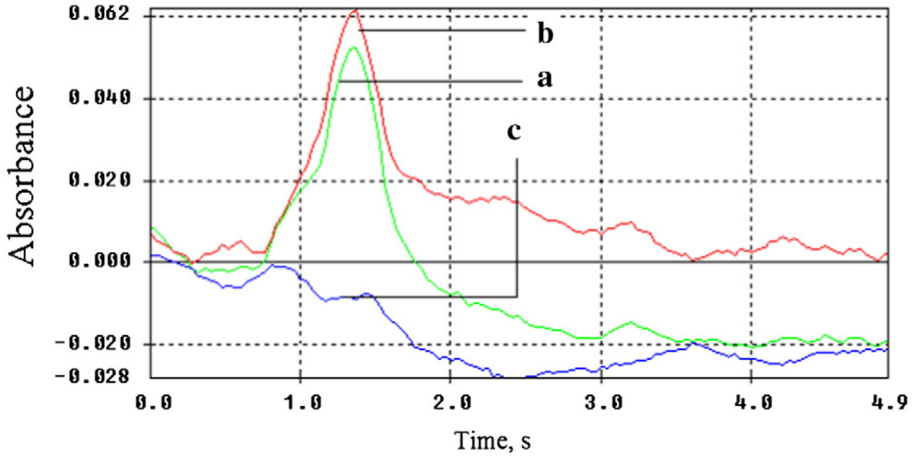

Fig. 2. Signal for 20.0 ng mL^{-1} Bi solution; total signal (a), corrected signal (b), D_2 background absorption signal (c) using W-coated SQT-AT-FAAS with the conditions in Table 2.

was employed and three replicate measurements were done under the optimum conditions. Certified and experimental values were 14.09 ± 0.15 ng mL^{-1} and 12.66 ± 1.12 ng mL^{-1}. As seen from the values, results were in good agreement with the certified value. There was no significant difference at 95% confidence level using Student's *t*-test.

Concentrations of Bi in two different tap water samples and Tigris River water were also determined by W-coated SQT-AT-FAAS method developed. Bismuth was not detected in tap water samples while 12.13 ± 1.15 ng mL^{-1} of Bi was found in Tigris River water. In our previous study, concentration of Bi had been found as 12.0 ± 0.6 ng mL^{-1} while it was not detectable in natural and top water samples.

4. Conclusion

Sensitivity of FAAS was improved for the determination of bismuth by using metal coated SQT and in situ atom trapping. Inner surface of double slotted quartz tube was coated with non-volatile metals, Mo, Zr, W and Ta, to improve the trapping efficiency of SQT. It was observed that W-coated SQT was more effective than others. Enhancement was found as 4.0 versus conventional FAAS. In situ atom trapping of Bi was also performed on W-coated SQT-AT-FAAS. All of the parameters were optimized to obtain best sensitivity. 613 fold enhancement in sensitivity was obtained by W-coated SQT-AT-FAAS with respect to FAAS with 5.0 min of trapping period and 5.5 mL min^{-1} of suction rate. LOD value was found to be 0.51 ng mL^{-1}. Accuracy was tested by using NIST-1643e and it was satisfactory. Bismuth was also determined in real sample using the method developed. Interferences are not too high in general, so external calibration could be used in the cases of SRM and real sample analyses. The method is suggested for bismuth determination as an alternative approach to sensitive techniques such as ETAAS and ICP-MS in laboratories where only a flame AAS instrument is available. An analysis period of a little more than 5.0 min is comparable to ETAAS; no long and involved procedures are involved in this in situ preconcentration technique. The procedure is simple and does not require any costly equipment.

Table 4
Comparison of detection limits for different techniques in Bi determination.

LOD[a]	Technique	Reference
0.12	Complexation of Bi(III) with 8-hydroxyquinoline and cloud point extraction using Triton X-100 prior to ICP-OES determination	[4]
0.15	EC-HG-AFS	[24]
3.8	Quartz tube atomizer with tungsten coil system coupled to FI-HG-AAS	[25]
0.4	Hydride generation integrated atom trap atomizer with flame atomic absorption spectrometry	[26]
0.07	Atmospheric pressure dielectric barrier discharge atomizer for Bi determination with HG-AFS	[27]
0.0027	Resistively heated W-trap for trapping of BiH_3 prior to its determination by AAS using a flame heated quartz tube atomizer	[28]
0.0039	Externally heated quartz tube atomizer for in situ trapping of BiH_3	[29]
0.16	Hydride generation ICP-OES determination of bismuth	[30]
0.51	W-Coated SQT-AT-FAAS	This study

[a] ng mL^{-1}.

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