



# Indium determination using slotted quartz tube-atom trap-flame atomic absorption spectrometry and interference studies

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## ABSTRACT

Sensitivity enhancement of indium determination by flame atomic absorption spectrometry (FAAS) was achieved; using a slotted quartz tube (SQT-FAAS) and slotted quartz tube atom trap (SQT-AT-FAAS). SQT was used as an atom trap (AT) where the analyte is accumulated in its inner wall prior to re-atomization. The signal is formed after re-atomization of analyte on the trap surface by introduction of 10  $\mu\text{L}$  of isobutyl methyl ketone (IBMK). Sensitivity was improved 400 times using SQT-AT-FAAS system with respect to conventional FAAS and 279 times with respect to SQT-FAAS without any collection. Characteristic concentration ( $C_0$ ) and limit of detection values were found to be 3.63  $\text{ng mL}^{-1}$  and 2.60  $\text{ng mL}^{-1}$ , respectively, using a sample flow rate of 7.0  $\text{mL min}^{-1}$  and a collection period of 5.0 min. In addition, interference effects of some elements on indium signal were studied. In order to characterize indium species trapped, X-ray Photoelectron Spectrometry (XPS) was utilized and it was found that indium was collected on the inner surface of SQT as  $\text{In}_2\text{O}_3$ . The accuracy of the procedure was checked to determine indium in the standard reference material (Montana Soil, SRM 2710).

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## 1. Introduction

Following its introduction by Walsh [1], atomic absorption spectrometry (AAS) was employed mostly with flame atomizers, namely the air/acetylene and nitrous oxide/acetylene flames; thus this technique is often called flame atomic absorption spectrometry (FAAS). Another commonly used atomization technique is using energy generated by resistive heating of a graphite cuvette for analyte atomization; this approach has been introduced by L'vov [2] and is called today as graphite furnace (GFAAS) or electrothermal atomic absorption spectrometry (ETAAS). A quartz tube heated by flame or resistance wires is another commonly used atomizer in hydride generation atomic absorption spectrometry (HGAAS); principles and applications on HGAAS have been reported in detail in a well-known monograph [3]. Principles, developments and applications of AAS using a variety of techniques have been reported in detail [4].

In FAAS, a nebulizer is used to produce fine droplets. It was reported that typical nebulisation efficiency that is the ratio of the sample amount transported to flame to the sample amount introduced to nebulizer is in the range of among 1–10% [5]. Therefore, a significant part of the sample is not transported to the atomizer.

For this reason, several analytical techniques have been used to improve the sensitivity of FAAS; these approaches have been given in a useful review paper by Matusiewicz [6].

One of the attempts to improve the sensitivity of FAAS was suggested by Watling [7,8]; a quartz tube with two slots was placed on flame and the atomization signal was monitored in this tube by using ordinary nebulisation. As one of these slots was designed to allow the laminar flame in, the upper one was also found to be necessary for reduced turbulence. The angle between these slots may be 120° or 180°. For some elements such as Ag, As, Bi, Cd, Pb Sb, Se, and Sn, the increase in sensitivity was 2–5 fold depending on the element. Among the reasons suggested to improve the sensitivity are reduced flame speed, longer optical path and the increased lifetime of free analyte atoms in flame [8]. This device and the relevant technique will be called slotted quartz tube (SQT) and SQT-FAAS, respectively, in this text. SQT-FAAS has been used by many laboratories equipped with FAAS and still finds some applications in recent years with a flame atomizer has had popularity in recent years in the scientific journals [9–13]. Among these recent reports, a sensitivity increase for lead and cadmium was obtained as high as 6 and 10 fold, respectively [11]. In the studies reported by Chinese workers, SQT was employed for Cr determination following preconcentration by cloud point extraction for water [12] and soil [13] samples.

A water cooled U-tube atom trap was introduced by Canadian researchers soon after the introduction of SQT [14]. As SQT could be used with ordinary sample nebulisation to provide an increase

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in continuous signal intensity, the U-tube technique involved trapping of analyte atoms on water-cooled quartz tube surface which was followed by the heating of the surface to effect atomization; therefore, a peak-shaped signal was used. This atom trap was simply an on-line enrichment technique where the quartz surface acts as the preconcentrator. Another important development was the use of U-tube trap in an SQT; this device was named as an integrated atom trap (IAT) [15]. In both the U-tube and IAT, cooling water was replaced by air and the resulting temperature increase resulted in re-atomization from the quartz surface; the signal was then obtained. Another way of releasing analyte species from the surface of silica was presented in 1993 [16]. In this work, instead of replacing water flow by air, it was suggested that the composition of the flame should be momentarily altered to effect fast re-atomization; the authors called this process as flame alteration [16]. The flame alteration approach was applied to SQT device by a Chinese group [17]. The same research that used flame alteration for the first time, proposed another and simpler way of revolatilization that is called organic solvent aspiration/atomization [18] which was used in these studies afterwards where the revolatilization mechanisms [19] and interferences [20] involved in SQT atom trap FAAS (SQT-AT-FAAS) were studied. In organic solvent aspiration technique, 10–50  $\mu\text{L}$  of an organic solvent, most often isobutyl methyl ketone (IBMK), is introduced and nebulised into the flame; the momentary change in the flame fuel/oxidant ratio is believed to be the reason of re-atomization from the quartz surface [18,19]. From these studies, SQT-AT-FAAS has evolved as an efficient alternative for sensitivity enhancement with FAAS. The sensitivity improvements reported by using SQT-AT-FAAS is 100 fold or higher. Developments in atom traps with particular emphasis on SQT have been recently reviewed [21,22].

In this study, a sensitive analytical method for indium determination will be reported by using SQT-FAAS and then SQT-AT-FAAS. To the best of our knowledge, this is the first study involving determination of indium, interference studies of some elements on indium signal by SQT-AT-FAAS and also analysis of indium species on quartz surface by X-ray photoelectron spectroscopy (XPS) in literature. A recent study involves the use of hydride generation and IAT [23].

## 2. Experimental

### 2.1. Apparatus and material

A 15.0 cm long SQT with two slots positioned at  $180^\circ$  with respect to each other was used; lengths of the lower and upper slots (thickness of both slots was 1.0 mm) were 100 mm and 80 mm, respectively; inner diameter of the tube was 13 mm and the outer diameter was 17 mm as shown in Fig. 1. For only the XPS surface studies, a small flat piece of quartz was placed in SQT to be handled as the sample so that it would not be necessary to break the quartz

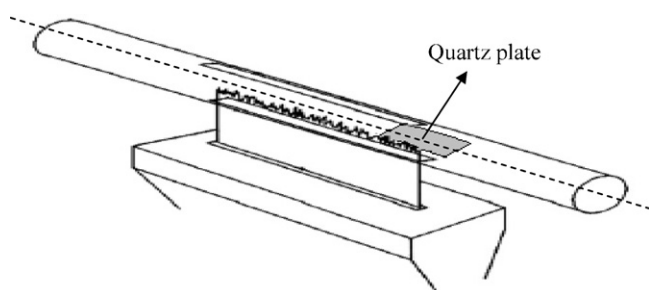


Fig. 1. The SQT device with two slots positioned at  $180^\circ$  with respect to each other.

tube for surface investigations. Otherwise, in a normal usage of it, there is no quartz piece in it.

### 2.2. Chemicals and reagents

Standard solution of 1000  $\text{mg L}^{-1}$  indium (Fisher Scientific International Company) was used for the preparation of working solutions. Intermediate standard solutions of indium were prepared by diluting the indium standard solution, using 18  $\text{M}\Omega\text{ cm}$  deionized water obtained from a Millipore (Molsheim, France) Milli-Q water purification system which was fed by the water produced by Millipore Elix 5 electro deionization system. All the standard solutions were prepared in 3.0  $\text{mol L}^{-1}$  HCl; for this purpose analytical grade of 37% HCl (Merck) was used. Multi-range Eppendorf micropipettes were used for preparation of solutions. Polyethylene containers with the capacity of 100 mL were used to store the solutions which were kept in refrigerator. For the aspiration of organic solvents into flame, 1.0 mL polyethylene cups were used.

All the glass and polyethylene containers were cleaned in 10% (v/v)  $\text{HNO}_3$  solution in a cleaning tank by immersing them for at least overnight. Cleaned materials were then washed with deionized water before use.

For the studied interferences, standard solutions used were in 1000  $\text{mg L}^{-1}$  for each element; namely, Fe (Merck), Co (High Purity Standards), Ni (High Purity Standards), Zn (High Purity Standards), Cd (High Purity Standards), As (Merck), Se (High Purity Standards), Hg (Merck), Tl (High Purity Standards), Sb (Ultra Scientific), Sn (Merck), Ca (Merck), Pb (Ultra Scientific), Ag (High Purity Standards) and Ir (Merck). All the solutions prepared for interference study contained 3.0  $\text{mol L}^{-1}$  HCl optimized.

### 2.3. Atomic absorption spectrometer and slotted quartz tube

An ATI Unicam 929 single beam atomic absorption spectrometer equipped with deuterium background correction was used. The results were saved using the software of the AA instrument. A stoichiometric air/acetylene type flame was used with a burner head of 100 mm. Philips data coded indium hollow cathode lamp with an operating current of 10 mA was used as the radiation source. All the analyses were done at the wavelength of 303.9 nm and a spectral band pass of 0.7 nm.

### 2.4. Surface study by X-ray photoelectron spectroscopy

The chemical nature of trapped indium was investigated on quartz surface using XPS. For this purpose, 1.0 mm thick flat quartz pieces with a length of 20.0 mm and a width of 10.0 mm were used. These quartz pieces were placed into the SQT as shown in Fig. 1. In the presence of a lean flame, 100.0  $\text{ng mL}^{-1}$  indium standard solutions were nebulised and part of the analyte was consequently trapped on these quartz pieces for 3 min. During this stage, suction rate of sample was 7.0  $\text{mL min}^{-1}$ .

SPECS ESCA system, at Middle East Technical University, Central Laboratory, with Mg/Al dual mode was used for the analysis of the quartz surface. Analyzer of spectrometer was EA 200 hemispherical electrostatic energy analyzer equipped with multichannel detector with 18 discrete channels. Unmonochromatized Mg K $\alpha$  radiation was used as the X-ray source, X-ray gun was operated at 10.0 kV, 20.0 mA and for excitation of indium on quartz, 278.0 W energy was used. Spectrometer was operated in constant analyzer energy mode. Pressure of analyzer chamber was kept in between  $10^{-8}$  and  $10^{-9}$  Torr. Atomic compositions were estimated using SpecsLab software. C (1s) signal was used as an internal energy calibrant at 284.5 eV binding energy.

**Table 1**Analytical performance for indium with FAAS, SQT-FAAS and SQT-AT-FAAS collection time was 5.0 min using sample suction rate of 7.0 mL min<sup>-1</sup> for SQT-AT-FAAS.

Methods	<sup>a</sup> LOD (ng mL <sup>-1</sup> )	<sup>b</sup> LOQ (ng mL <sup>-1</sup> )	C <sub>0</sub> (ng mL <sup>-1</sup> )	<sup>c</sup> E	
				With respect to FAAS	With respect to SQT-FAAS
FAAS	8.6 × 10 <sup>2</sup>	2.58 × 10 <sup>3</sup>	1.45 × 10 <sup>3</sup>	1	–
SQT-FAAS	6.0 × 10 <sup>2</sup>	1.80 × 10 <sup>3</sup>	1.01 × 10 <sup>3</sup>	1.43	1
SQT-AT-FAAS	2.60	7.80	3.63	400	279

<sup>a</sup> Three times the standard deviation of 11 replicate signals using the lowest value in the working range.<sup>b</sup> Nine times the standard deviation of 11 replicate signals using the lowest value in the working range.<sup>c</sup> E, enhancement, is based on the ratio of characteristic concentration (C<sub>0</sub>) values.

### 2.5. Preparation of standard reference material

0.5 g of standard reference material (Montana Soil, SRM 2710) were digested with a mixture of 4 mL of 37% HCl, 4 mL of 64% HNO<sub>3</sub> and 2 mL of 49% HF in a microwave digestion system. The resulting solution was diluted with deionized water to 50 mL in a volumetric flask.

## 3. Results and discussion

### 3.1. Flame atomic absorption spectrometry (FAAS)

In the preliminary stages of this study, determination of indium was performed by conventional FAAS technique without any SQT device for sensitivity improvement. Some of the analytical parameters such as observation height (O.H.) i.e. the distance between the top of the flame head and the centre of the optical beam cross section and sample flow rate was optimized in order to obtain better S/N ratio. Optimization studies were carried out by using 20.0 mg L<sup>-1</sup> indium standard solution. The optimization was made in several cycles until the result obtained did not differ from the last optimum value. During any optimization, as the value of the parameter in question was varied, all the other parameters were in their optimized values. The optimum values for O.H. and the sample flow rate were found to be 20 mm and 7.0 mL min<sup>-1</sup>, respectively.

Using the optimized parameters, absorbance values of indium solutions in concentrations between 2.0 and 50.0 mg L<sup>-1</sup> were measured. In this part of the study, calibration plot was linear between 2.0 and 25.0 mg L<sup>-1</sup>. The best line equation and correlation coefficient were,  $A = 0.00212C + 0.00753$  and 0.9982, respectively. In this equation, C is the indium concentration in mg L<sup>-1</sup>, and A is the absorbance. The points on the calibration plot are based on the average of triplicate readings for each standard solution.

Limit of detection (LOD), limit of quantitation (LOQ) and characteristic concentration (C<sub>0</sub>) were found as 8.60 × 10<sup>2</sup>, 2.58 × 10<sup>3</sup> and 1.45 × 10<sup>3</sup> ng mL<sup>-1</sup>, respectively, as shown in Table 1. In order to determine LOD and LOQ, 11 measurements taken for 2.0 mg L<sup>-1</sup> indium solution were used.

### 3.2. Slotted quartz tube-flame AAS (SQT-FAAS)

When the SQT-FAAS was used, the sensitivity of FAAS was enhanced. SQT should be positioned on the burner head of instrument carefully so that this position allows the entire light beam pass through the tube. Flame is allowed to enter through the lower slot into SQT. Absorbance measurements are taken while the sample solution is aspirated continuously. In order to find the best analytical sensitivity, sample suction rate and height of SQT from the burner head were optimized by using 20.0 mg L<sup>-1</sup> indium solution. For optimizations, a univariate approach as explained in FAAS section was undertaken to establish the best conditions for indium determination.

During the optimization, when the suction rate of sample was increased, absorption signal became higher. This is expected

because of increased population of analyte atoms per unit time in flame. Excessively high flow rates were avoided. Selected suction rate for indium solution was found to be 7.0 mL min<sup>-1</sup>. Height of SQT with respect to burned head of flame is also another important experimental parameter to be optimized; it was varied from 4.0 mm to 10.0 mm and 7.0 mm was found to be the optimum value to give the best signal.

Using the optimum experimental parameters given above, linear calibration plot with SQT-FAAS method for indium was constructed between 2.0 and 50.0 mg mL<sup>-1</sup>. The best line equation and correlation coefficient were,  $A = 0.00372C + 0.00672$  and 0.9996, respectively. LOD, LOQ and C<sub>0</sub> values are shown in Table 1. Sensitivity enhancement of SQT-FAAS method with respect to FAAS was 1.43 fold when C<sub>0</sub> values were compared.

### 3.3. Slotted quartz tube atom trap flame AAS (SQT-AT-FAAS)

In this section of study, SQT was used as an atom trap device in which analyte species are trapped on the inner surface of this device. In this system, SQT is placed above the flame in a way similar to SQT-FAAS. Sample solution containing analyte of interest is aspirated. *Collection step*, during which analyte atoms are trapped on the inner surface of SQT can be continued for a few minutes as desired. After the collection step of a time period chosen, aspiration is stopped and small volume of organic solvent (10–50 µL) is aspirated into flame. This stage is called as *revolatilization step*. Organic solvent momentarily alters the flame composition and trapped analyte species are released from the surface of quartz; a transient signal is obtained, peak height is measured [18,19,22].

In this study, in order to obtain better sensitivity, some analytical parameters such as acidity of sample solutions, suction rate of sample, both type and amount of organic solvent, and the distance between SQT and burner head were optimized. Position of two slots on SQT with respect to each other and influence of trapping period were also studied.

#### 3.3.1. Optimization of acidity of sample solutions

In the preliminary of the study, different types of acids which are HNO<sub>3</sub>, H<sub>2</sub>SO<sub>4</sub> and HCl have been tested to obtain better sensitivity. By the time H<sub>2</sub>SO<sub>4</sub> was used, indium signal was not taken. In the case of using HNO<sub>3</sub>, sensitivity of indium was around 3 times lower than HCl. Because of this reason, in this study, indium standard solutions were prepared in aqueous HCl solution. In order to find the optimum HCl concentration, its concentration in the analyte solution was varied between 0 and 5.0 mol L<sup>-1</sup>. The optimum value for HCl was found to be 3.0 mol L<sup>-1</sup>, somewhat in the middle of the plateau of the curve when an optimization graph was plotted. Values higher and lower than 3.0 mol L<sup>-1</sup> for HCl resulted in a gradual decrease in the analytical signal.

#### 3.3.2. Effect of sample suction rate

In principle, the amount of analyte collected for the unit time is directly related with the nebulisation efficiency. Suction rate of sample also affects the nebulisation efficiency. At low suction rates,

amount of analyte species aspirated into the flame becomes lower, but nebulisation efficiency increases resulting in higher trapping efficiency. On the other hand, suction rate affects the flame conditions during atomization in which an organic solvent is used. Therefore, excessively high values should be avoided. During the optimization,  $100 \text{ ng mL}^{-1}$  indium standard solutions were used with a 5.0 min for collection step. When the suction rate of sample was increased, total amount of analyte present in trapping zone per unit time and thus in the measurement zone becomes higher, resulting in a higher signal. When a constant time for sampling is used, higher suction rate is advantageous; however, when a constant sample volume is to be used, lower suction rate is better since the corresponding nebulisation efficiency is higher [18,19]. In this study, a constant sampling time of 5.0 min was used; therefore, higher suction rate should be preferred. The optimum suction rate of sample was found to be  $7.0 \text{ mL min}^{-1}$ .

### 3.3.3. Optimization of type of organic solvent

In order to strip trapped indium species from the surface of SQT, organic solvent aspiration was performed during the revolatilization [18]. Type of organic solvent is important for rapid revolatilization of analyte species from the surface. For this purpose, several types of organic solvents were used such as isobutyl methyl ketone (IBMK), methyl ethyl ketone, acetonitrile, isopropyl alcohol, ethyl alcohol, and cyclopentanol for indium determination. In cases of methyl ethyl ketone, acetonitrile, isopropyl alcohol, and cyclopentanol, no analytical signal was obtained indicating that these solvents did not alter the flame composition significantly. After trapping, analyte signal was obtained by ethyl alcohol but there was some memory effect; after aspiration of ethyl alcohol to obtain the analytical signal, subsequent blank injections of solvent gave small signals indicating that not all of the indium species were released from SQT surface during analytical signal. Therefore, when ethyl alcohol was used, several revolatilization stages had to be performed to make sure that all the trapped indium species were released from SQT surface. Hence, IBMK was selected further experiments since a good signal with no memory effect was obtained.

### 3.3.4. Optimization of volume of organic solvent

After the suitable organic solvent for revolatilization was chosen, its volume was optimized. In principle, in order to revolatilize the trapped analyte species from the surface of SQT, a small volume of organic solvent ( $10\text{--}50 \mu\text{L}$ ) is sufficient. In this study, volume of IBMK was varied from 10 to  $200 \mu\text{L}$ , and it was concluded that  $10 \mu\text{L}$  gave complete revolatilization of  $100.0 \text{ ng mL}^{-1}$  indium solution. Since higher volumes of organic solvent causes the extension of the momentarily formed fuel rich flame outside the ends of SQT approaching to the windows on both sides, the quartz windows of spectrometer may be damaged. Therefore,  $10 \mu\text{L}$  of IBMK was used for the rest of the study.

### 3.3.5. Optimization of height of the SQT from the burner head

In the SQT-FAAS section, when the height between burner head and SQT was increased too much, signal of indium decreased because indium atoms cannot be efficiently transported into SQT. This result was also valid for SQT-AT-FAAS method. For this purpose, height of the SQT from the burner head was varied between 4 mm and 10 mm, the best optimum distance was found to be 7.0 mm. It turns out that this is the same value used for SQT-FAAS.

### 3.3.6. Effect of position of two slots with respect to each other

In order to understand the effect of relative position of upper and lower slots of SQT with respect to each other, three different SQT devices were produced where two slots were positioned at  $90^\circ$ ,  $120^\circ$  and  $180^\circ$  with respect to each other. As shown in Fig. 2, when

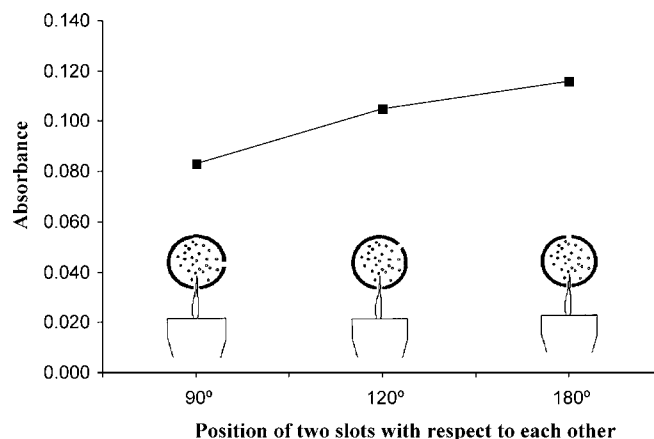


Fig. 2. Optimization of position of up and down slots of SQT with respect to each other (indium,  $100 \text{ ng mL}^{-1}$ ; collection time, 5.0 min; suction rate,  $7.0 \text{ mL min}^{-1}$ ).

two slots of SQT were positioned at  $180^\circ$ , indium signal was higher than others. Therefore, in further studies, experiments were carried out by using this  $180^\circ$  configuration for SQT.

### 3.3.7. Investigation of trapping period

If trapping is performed for a longer period, sensitivity of system is improved because more analyte species are trapped on the surface of SQT. On the other hand, SQT-AT-FAAS is to be competing with highly sensitive methods such as inductively coupled plasma mass spectrometry (ICP-MS) and electrothermal atomic absorption spectrometry (ETAAS); therefore time required for the analysis should be only a few minutes in order to eliminate the consumption of high amount of analyte solution. Exceedingly high sample volumes or long time periods reduce the attractiveness of inexpensive preconcentration procedures. In this study, effect collection period was tested between 1 and 15 min. Indium signal linearly increases up to 10 min, for longer periods the increase is not linear with a lower slope. By considering a reasonable analysis period and analyte solution to be consumed, collection period was chosen as 5 min in further studies.

### 3.3.8. Calibration plot for SQT-AT-FAAS method

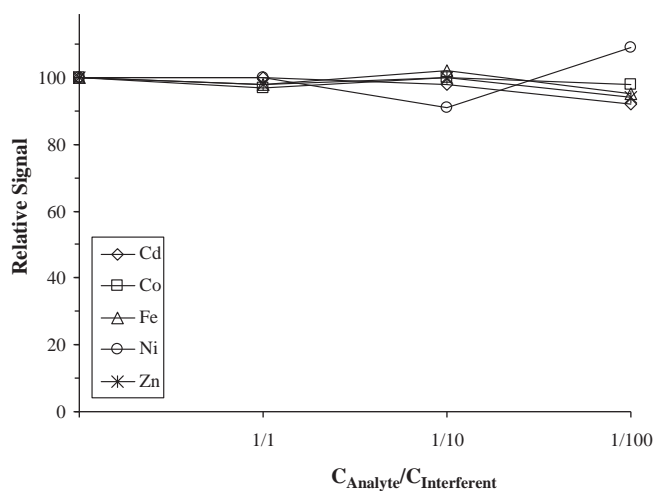
For linear calibration plot with SQT-AT-FAAS method, indium standards between  $0.010$  and  $0.250 \text{ mg L}^{-1}$  were used. The best line equation and correlation coefficient were,  $A = 0.00104C + 0.00525$  and  $0.9983$ , respectively. LOD, LOQ and  $C_0$  values of this technique are shown in Table 1. When compared the  $C_0$  values, 400 and 279 fold sensitivity enhancements were obtained with respect to FAAS and SQT-FAAS methods, respectively. In this case, volume of indium solution consumed was 35 mL, using a suction rate of  $7.0 \text{ mL min}^{-1}$  and a collection period of 5.0 min.

## 3.4. Evaluation of system performance

In general, by comparing the  $C_0$  values of two methods, sensitivity enhancement ( $E$ ) can be found.  $E$  also means the ratio of calibration sensitivities (slopes). Ataman [22] introduced two new terms, enhancement factors in terms of unit time,  $E_t$ , and unit volume,  $E_v$ .  $E_t$  is obtained by dividing  $E$  value by the total time spent in terms of minutes, and  $E_v$  is obtained by dividing  $E$  value by the total volume spent in units of milliliter. Therefore, it would be possible to make a fair comparison of two methods using the terms of the trapping period and the total amount trapped. In this study, for SQT-AT-FAAS method,  $E_t$  and  $E_v$  values are shown in Table 2 with respect to FAAS and SQT-FAAS for indium determination.

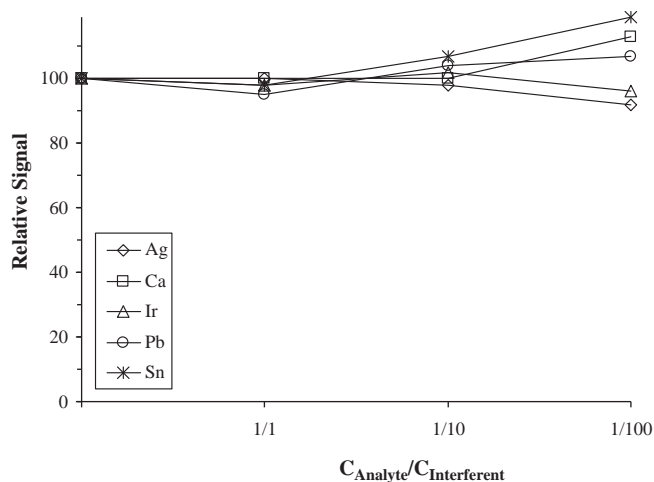
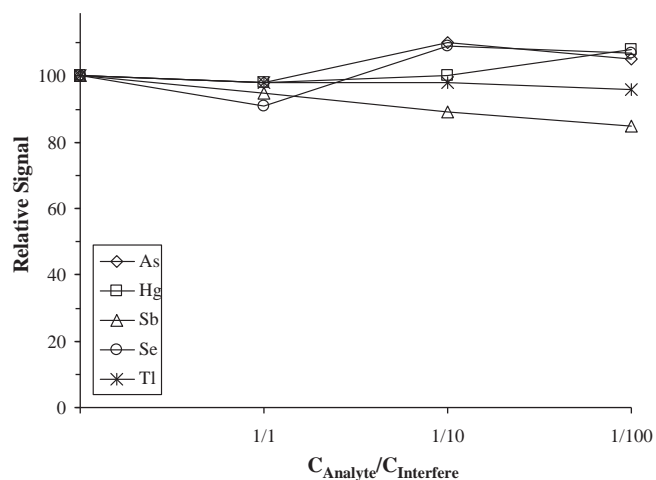
**Table 2**Enhancement for SQT-AT-FAAS in terms of  $E$ ,  $E_t$  and  $E_v$  values.

	Sensitivity enhancement normalized to unit time or unit volume		Sensitivity enhancement, $E$
	<sup>a</sup> $E_t$ ( $\text{min}^{-1}$ )	<sup>b</sup> $E_v$ ( $\text{mL}^{-1}$ )	
With respect to FAAS	80	11	400
With respect to SQT-FAAS	56	8.0	279

<sup>a</sup>  $E_t = E/5.0$  min.<sup>b</sup>  $E_v = E/35$  mL.**Fig. 3.** Interference effects of Cd, Co, Fe, Ni and Zn on Indium signal (indium,  $100 \text{ ng mL}^{-1}$ ; collection time, 2.0 min; suction rate,  $7.0 \text{ mL min}^{-1}$ ).

### 3.5. Interference studies of some elements on indium signal with SQT-AT-FAAS method

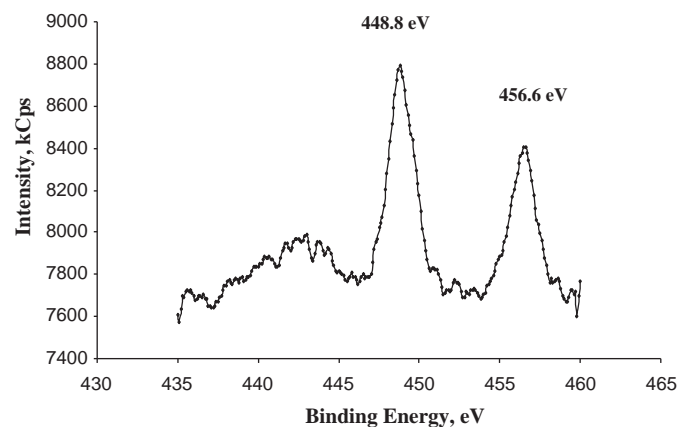
In order to investigate the effects of some other elements on indium signal, interference studies were performed. For this reason, 3 different solutions were prepared in which the concentration of indium was kept constant as  $100.0 \text{ ng mL}^{-1}$ , and concentrations of interferences were 1, 10 and 100 fold of the analyte concentration, using the mass ratios. Since the solutions are prepared in  $3.0 \text{ mol L}^{-1}$  HCl; counter ion should be chloride for cations where the counter cation is hydrogen ion for anionic analyte species. Interference effects of Ag, As, Ca, Cd, Co, Fe, Hg, Ir, Ni, Pb, Sb, Se, Sn, Tl and Zn on indium signal have been investigated by using a collection period of 2.0 min and results are shown in Figs. 3–5. As seen

**Fig. 4.** Interference effects of Ag, Ca, Ir, Pb, and Sn on Indium signal (indium,  $100 \text{ ng mL}^{-1}$ ; collection time, 2.0 min; suction rate,  $7.0 \text{ mL min}^{-1}$ ).**Fig. 5.** Interference effect of As, Hg, Sb, Se and Tl on Indium signal (indium,  $100 \text{ ng mL}^{-1}$ ; collection time, 2.0 min; suction rate,  $7.0 \text{ mL min}^{-1}$ ).

from Fig. 3, Cd, Co, Fe and Zn do not affect the indium signal significantly at given proportions; Ni causes an enhancement by about 10% at the lowest analyte/interference ratio. On the other hand, in the case of Sn as shown in Fig. 4, when the analyte/interference is 1/100, indium signal is enhanced around 20%. In the case of Sb shown in Fig. 5, when the analyte/interference is 1/100, indium signal is decreased by around 20%; the other elements in this group have lower effect on analyte signal. These results indicate that the procedure can be applied satisfactorily for indium determination in a variety of matrices.

### 3.6. Chemical state of indium on quartz surface

Indium ( $3d_{3/2}$ ) and indium ( $3d_{5/2}$ ) peaks are shown in Fig. 6 which are at 456.6 eV and 448.8 eV, respectively. In this study, C (1s) peak was used as an internal energy calibrant at 284.5 eV bind-

**Fig. 6.** XPS spectrum of In(3d) on quartz surface (indium,  $100 \text{ ng mL}^{-1}$ ; collection time, 5.0 min; suction rate,  $7.0 \text{ mL min}^{-1}$ ).

**Table 3**

Atom percentages and orbitals of elements on SQT after trapping indium.

Element	Atom (%)	Orbital
C	9.9	1s
O	70.7	1s
Si	19.1	2p
In	0.3	3d <sub>5/2</sub>

ing energy. C (1s) peak was observed at 288.1 eV; thus C (1s) shift was found to be +3.6 eV. By subtracting the C (1s) shift from these peaks of indium (3d<sub>3/2</sub>) and indium (3d<sub>5/2</sub>), true indium (3d<sub>3/2</sub>) and indium (3d<sub>5/2</sub>) peaks were found as 453.0 eV and 445.2 eV, respectively. These peaks are assigned to +3 oxidation state of indium [24]. Hence, oxidation state of indium on quartz surface during trapping period was found to be 3+. Amounts of carbon, oxygen, silicon and indium during the analysis of quartz sample consisting of indium are shown in Table 3 in which indium surface atom percentage is 0.3%.

### 3.7. Accuracy check for SQT-AT-FAAS method

The standard reference material (SRM 2710, Montana Soil) was used for the accuracy check of SQT-AT-FAAS method. The direct calibration was employed and six replicate measurements were done under optimum conditions. The noncertified and found values were 5.10 and  $5.14 \pm 0.06 \text{ mg kg}^{-1}$ , respectively. As shown, the results were in good agreement between each other.

## 4. Conclusions

The aim of this study is to enhance the sensitivity of FAAS by using SQT as an atom trap for indium determination. To the best of our knowledge, this is the first study to report indium determination using SQT-AT-FAAS and investigate both interference effects of some elements on indium signal and the chemical state of indium on quartz surface in literature.

The method described in this article requires very simple and inexpensive equipment. Only a simple AA spectrometer with a flame atomizer is needed as the major instrument. SQT device can very easily be produced in any glass shop with almost no cost.

A single measurement takes a little more than 5.0 min, the collection period adapted in this study, since the aspiration of 10  $\mu\text{L}$  IBMK and the acquisition of signal can be accomplished in less than 30 s. Shorter periods can be employed at reduced sensitivity. Time spent is comparable to that is needed in an ETAAS measurement;

however, the volume required is definitely significantly higher. The limit of detection,  $2.60 \text{ ng mL}^{-1}$ , is sufficiently low so that the method would be applicable for many applications. There are no significantly high interference effects. SQT-AT-FAAS for indium determination seems to be a powerful and simple candidate at a low cost. This developed method for indium determination was tested successfully for SRM 2710, Montano Soil without any interference. Therefore, this method can be easily applied for including difficult sample matrixes such as alloys, mining, rock and soil samples.

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