

Speciation and determination of thallium by on-line microcolumn separation/preconcentration by flow injection–flame atomic absorption spectrometry using immobilized oxine as sorbent

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A flow injection analysis (FIA) system incorporating a microcolumn of immobilized oxine on surfactant-coated alumina had been devised for performing rapid thallium enrichment/matrix removal in flame atomic absorption spectrometry (FAA). The preconcentration is based on the deposition of thallium(I) on the microcolumn and subsequent elution with 500 μl of sodium thiosulfate (1 mol l^{-1}). In the presence of EDTA, only Tl(I) was retained on the microcolumn. Total thallium was determined after reduction of Tl(III) to Tl(I) by hydroxyl amine hydrochloride. A sample volume of 25 ml resulted in a preconcentration factor of 77. Precision at $30 \mu\text{g l}^{-1}$ was 2.6% RSD ($n = 10$). With 25 ml sampling volume a detection limit of $2.5 \mu\text{g l}^{-1}$ was determined. The effect of potential interfering ions on the determination was studied. The method was applied for the determination of thallium in water, waste water, hair, nail, coal, and standard reference alloys. The accuracy was assessed through recovery experiment, independent analysis by Furnace-AAS, and analysis of certified reference alloys.

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1. Introduction

Thallium is a heavy metallic element that exists in the environment mainly combined with other elements (primarily oxygen, sulfur and the halogens) in inorganic compounds. Thallium can be found in nature as Tl(I) and Tl(III) ions but its monovalent state has higher stability, whereas its trivalent state forms complexes of greater stability. Thus each redox state of the element exhibits different bioavailability and toxicity property [1]. Therefore speciation of thallium in environment is important. However as the total concentration of thallium in aquatic environment is very low an analytical technique featuring high sensitivity and low detection limit is required. Inductively coupled plasma mass spectrometry (ICP-MS) [2–4] laser-excited atomic fluorescence spectrometry (LEAFS) [5] and electrothermal atomic absorption spectrometry [6–10] (ETAAS) had been used for determination of thallium, but ICP-MS is an expen-

sive analytical method and incurs high running cost, LEAFS is less frequently used technique and direct analysis with ETAAS involves many difficulties because of spectral and nonspectral interferences [11].

Flame atomic absorption spectrometry (FAAS) is a simple and well available technique for determination of thallium in real samples. However its main problem is the low sensitivity for trace determination at $\mu\text{g l}^{-1}$ level. This limitation can be overcome by the use of a preconcentration procedure. For this purpose various preconcentration/separation methods including liquid–liquid extraction [12], hydride generation [13], solid phase extraction [14–17] and flotation [18] had been used. However, these manual batch procedures are labor, time and reagent consuming, and require large volume of sample.

Flow injection (FI) separation and preconcentration provide valuable tools for the automation of analytical procedures and are effective for enhancing sensitivity of atomic spectrometry. However, to the best of our knowledge there are few reports on automation of determination of Tl with FAAS [19–22]. Shukun and coworkers [19] developed a flow injection vapor generation atomic absorption spectrometric (FI-VGAAS) for enhancing

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response signals of copper, gold and thallium. Mohammad et. al [20] studied the complexation chemistry and speciation of thallium for on-line preconcentration with immobilized quinolin-8-ol. With a 5 cm column and 3 min preconcentration time a detection limit of 3 ng ml^{-1} and a concentration factor of 55 for Tl^{3+} was reported. Tang and coworkers [21] also developed a flow injection–on-line extraction flame atomic absorption spectrometry for determination of thallium in geochemical samples. Ratka and coworkers [22] reported that diaphragm pump can be used for on-line sample preconcentration and matrix separation in flame AAS and ICP-OES by using HPLC pre-column or small ion exchange columns. They claimed that for several metals including thallium very low detection limit in flame AAS was achieved, however their main aim was development of a novel analytical low cost flow system based on a 0.6 MPa (84 psi) diaphragm pump. Thus development of a FI-FAAS method for selection separation, preconcentration, speciation, and determination of thallium is still a challenging area of research.

8-Hydroxyquinoline (oxine) is a classical group reagent, often applied to the precipitation or liquid extraction of a large number of elements. It forms complexes with metal ions through the formation of a chelate ring in the basic nitrogen and phenolic group. Oxine had been chemically immobilized on supports such as Amberlite XAD series [19,23], cellulose [24–28] silica gel [29,30], and chitosan [31–33] to affect separation and preconcentration of trace metals from different matrices. In this work oxine had been physically immobilized on surfactant-coated alumina and its capability for on-line trace enrichment of thallium ion was investigated. Studies confirmed the reliability of microcolumn enrichment/separation using immobilized oxine as the sorbent, and a simple, rapid method based on FI-FAAS has been developed for preconcentration, speciation and determination of thallium at trace level.

2. Experimental

2.1. Reagents

All chemicals and solvents were analytical reagent grade, which were used without further purification. Double deionized water was used throughout. A stock solution (100 mg l^{-1}) of Tl^+ and Tl^{3+} was prepared by dissolving an accurate weight of either TlNO_3 (Merck, Germany) or $\text{Tl}(\text{NO}_3)_3 \cdot 3\text{H}_2\text{O}$ (Merck, Germany) into a 100 ml flask and diluting to the mark with distilled water. Standard solution were prepared daily from the stock solution by serial dilution with water. Sodium thiosulfate solution (1 mol l^{-1}) was prepared by dissolution of 25.06 g of $\text{Na}_2\text{S}_2\text{O}_3 \cdot 5\text{H}_2\text{O}$ into 100 ml flask and diluting to the mark with water.

Alumina ($10\text{--}50 \mu\text{m}$, γ -type chromatography grade, Merck, Darmstadt, Germany) was purified by shaking with 5 mol l^{-1} nitric acid and washing three times with water. Sodium dodecyl sulfate (SDS) (Merck, Darmstadt, Germany), and 8-hydroxyquinoline (oxine) (Merck, Darmstadt, Germany) was used without further purification. A 0.1% solution of oxine was prepared by dissolving 100 mg of oxine in acetone. Reagent

blank was prepared by processing a solution of 1 mol l^{-1} sodium thiosulfate (eluent) through a column of immobilized oxine.

2.2. Instrumentation

A Buck Scientific atomic absorption spectrometer (model 210 VGP, USA), furnished with Tl hollow-cathode lamps and air-acetylene flame was used for all measurements. The operating conditions were as follows—wavelength: 276.8 nm , slit width: 0.7 nm and lamp current: 10 mA . The absorbance time response was monitored on an $x-t$ chart recorder (linseis model L-250) and quantitative analysis was based on measurement of the peak height of transient signals. A schematic diagram of flow injection system used is presented in Fig. 1. The manifold consists of peristaltic pump (Ismatec, Ms-4 REGLO/8-100, Switzerland), rotary injection valve (Rheodyne, California, USA) and microcolumn of oxine immobilized on surfactant-coated alumina (PTFE tube $4 \text{ cm} \times 2 \text{ mm i.d.}$).

2.3. Preparation of the sorbent and microcolumn

Fifty milliliters of a solution ($\text{pH} \approx 5$) containing 100 mg SDS was added to 1.5 g of alumina. The solution was mixed with a magnetic stirrer for 10 min. The supernatant was decanted and the SDS-coated alumina was washed thoroughly with several portion of water. Then $\sim 20 \text{ ml}$ of water and $5\text{--}7 \text{ ml}$ of oxine solution (0.1 g dissolved in acetone) were added. The solution was shaken for 15 min. The mixture was then filtered through Millipore filter, washed, air-dried and was kept in close bottle before use. It was stable for more than 1 month. The resulting sorbent was characterized by employing Fourier transform infrared spectrometry (FTIR). The characteristic IR bands in cm^{-1} for immobilized oxine were: 1607.7 (C=N stretching in aromatic ring), 1474.1 and 1387.4 (skeleton bands of aromatic rings) 1284.6 (C–O stretching). These prove the loading of oxine on SDS coated alumina.

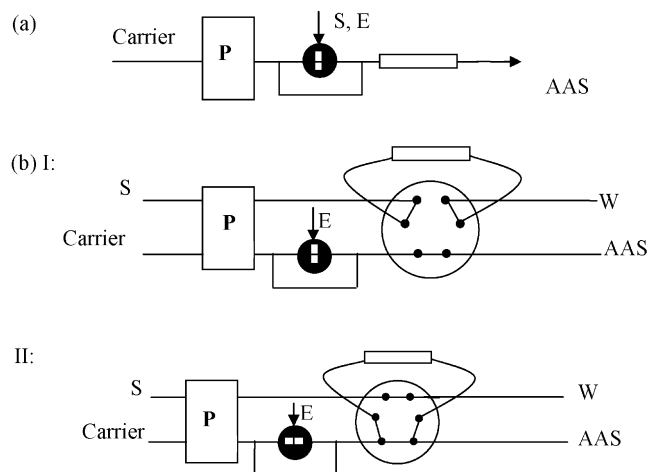


Fig. 1. Schematic diagram of the flow system used for pre-concentration and determination of thallium. (a) Single line FI system. (b) Two line FI system: (I) sample loading, (II) injection, (S) sample, (P) peristaltic pump, (C) microcolumn and (W) waste. Valve positions.

Microcolumn was fabricated by using PTFE (Teflon) tubing (4 cm in length, internal diameter of 2 mm) containing oxine immobilized on surfactant coated alumina (~80 mg). The end of the tube was fitted with foam to retain the sorbent in the tube.

2.4. Preparation of real samples

2.4.1. Hair and nail

The hair and nail sample was rinsed with acetone, chloroform and doubly distilled water, and was dried at 60 °C. Exact amount of dried sample (1 g for nail or 1.5 g for hair) was placed in three 50 ml beakers and 5 ml concentrated HNO₃ were added. The content of the beakers were heated on a hot plate (initially at 100 °C for 45 min and then at 150 °C for 15 min) after dissolution, the solution was cooled to 70 °C and 2 ml of 30% H₂O₂ was added. The mixtures were heated to dryness at 200 °C to yield a white residue.

Approximately 10 ml of 0.1 mol l⁻¹ HNO₃ was added to the beakers and the contents were heated at 100 °C for several minutes. Then 1.75 ml of hydroxylamine hydrochloride (0.1 mol l⁻¹) and 1.5 ml of EDTA (0.01 mol l⁻¹) was added, the pH was adjusted to ~6–7 with ammonium hydroxide solution (0.01 mol l⁻¹), and the content was diluted to 25 ml. The total thallium was determined according to the given procedure.

2.4.2. Water and wastewater

The samples were filtered through a Millipore filter, then to 40 ml of the sample 3.5 ml of hydroxylamine hydrochloride (0.1 mol l⁻¹) and 3 ml of EDTA (0.01 mol l⁻¹) was added, the pH was adjusted to ~6–7 with ammonium hydroxide solution (0.01 mol l⁻¹) and was diluted to 50 ml, then 25 ml of this solution was treated according to the given procedure.

For speciation of thallium in river water, to 40 ml of sample 3 ml of EDTA (0.01 mol l⁻¹) was added and the pH was adjusted to ~6–7 with ammonium hydroxide solution, the solution was diluted to 50 ml and was treated according to the given procedure.

2.4.3. Preparation of coal

To 2.5 g of coal, 5 ml nitric acid was added and the content was heated over the water bath for 1 h, then few milliliter of water was added and the solution was filtered. Then 1.75 ml of hydroxylamine hydrochloride (0.1 mol l⁻¹) and 1.5 ml of EDTA (0.01 mol l⁻¹) was added, the pH was adjusted to ~6–7 with ammonium hydroxide solution and the solution was diluted to 25 ml. The total thallium content was determined according to the given procedure.

2.4.4. Certified reference materials

To 0.1 g of BCR, No. 288 or CRM No. 5406-90, 5 ml of concentrated nitric acid was added. The solution was heated over a water bath for few minutes and 3 ml H₂O₂ was added. The solution was further heated for few minutes and was cooled and filtered. Then 3.5 ml of hydroxylamine hydrochloride (0.1 mol l⁻¹) and 3 ml of EDTA (0.01 mol l⁻¹) was added, and the pH was adjusted to ~6–7 with ammonium hydroxide solution. The solution was transferred to 50 ml flask, and was

diluted to mark upon addition of distilled water. Then 25 ml of this solution was treated according to the given procedure.

2.5. Procedure

The flow injection manifolds used were connected directly to the nebulizer inlet tubing and are presented in Fig. 1. The single line system (Fig. 1(a)) was used to study analyte breakthrough and to undertake initial method development studies. The two-line FI manifold (Fig. 1(b)) was used to process real samples and to obtain performance data. The carrier and eluent solution were water and sodium thiosulfate (500 μl, 1 mol l⁻¹), respectively. The microcolumn was located in the sample loop of injection valve, so that, sampling could be performed “off line” and preventing matrix constituents entering the AAS. At the end of sampling the valve was switch “on line” and the eluent was injected with the use of second valve to effect elution.

For measurement of total thallium, to 40 ml of sample, 3.5 ml of hydroxylamine hydrochloride (0.1 mol l⁻¹), and 3 ml of EDTA (0.01 mol l⁻¹; in order to mask ions which form complex with oxine) was added, the pH was adjusted to ~6–7 with ammonium hydroxide solution and was diluted to 50 ml. Whereas for measurement of thallium(I), to 40 ml of sample only 3 ml of EDTA (0.01 mol l⁻¹) was added, the pH was adjusted to ~6–7 with ammonium hydroxide solution and was diluted to 50 ml.

With reference to FI manifold (Fig. 1(a) and (b)), standard solution or samples were passed through the oxine microcolumn (Fig. 1(a)) sample volume 500 μl; Fig. 1(b) volume based sampling (e.g. 25 ml at flow rate of 3 ml min⁻¹) to effect deposition of the analyte. The adsorbed analyte was then eluted by injection of sodium thiosulfate (500 μl, 1 mol l⁻¹) and transported to flame atomic absorption spectrometer for quantization. (For the FI system in Fig. 1(b) the injection valve was switched to bring the microcolumn “on line” prior to the injection of eluent). The concentration of Tl(III) was calculated by the difference between the value of total thallium and thallium(I). The transient signals were monitored for quantitative analysis. Processing of 1 ml of carrier was necessary before commencement of the next deposition/elution cycle to reestablish the column.

3. Results and discussion

In 1994, Hiraide et al. [34] proposed that water-insoluble organic ligand could be trapped into the aggregate of sodium dodecyl sulfate (SDS) on alumina particles. Since then different organic ligands had been immobilized on surfactant coated alumina and had been used successfully as a column preconcentration media in batch [34–36] and FIA [37–39] system. In the preliminary studies it was found that when 0.2% solution of oxine in acetone is mixed with SDS coated alumina particles, the ligand is trapped homogeneously on the hemi-micelles or ad-micelles formed by SDS on alumina surface in a manner similar to that demonstrated for the other classical organic ligands [34–39] and the color of alumina was changed from white to yellow. Furthermore with the use of single line FI system (Fig. 1(a)) it was established that the prepared sorbent had the capability

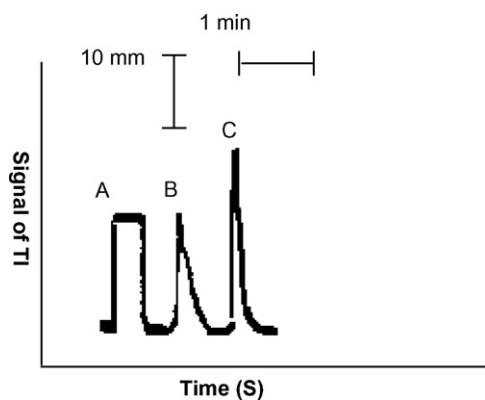


Fig. 2. Absorbance time response for: (A) conventional nebulization of 3 mg l^{-1} of Tl(I) in eluent matrix, (B) direct injection of Tl(I) solution ($500 \mu\text{l}$ of 3 mg l^{-1} eluent matrix) and (C) sequential injection of sample solution ($500 \mu\text{l}$) and eluent ($500 \mu\text{l}$ of sodium thiosulfate 1 mol l^{-1}) of Tl (I).

of retaining thallium (I) from sample aqueous solution. Thallium forms a 1:1 complex with oxine, through coordinate with oxygen and nitrogen donor atom.

A typical absorbance time response for the sequential injection of a standard solution ($200 \mu\text{l}$ of 3 mg l^{-1} thallium) and sodium thiosulfate ($500 \mu\text{l}$ of 1 mol l^{-1}) is given in Fig. 2C, and for comparison, the equivalent transient signals for direct injection and pneumatic nebulization of sample (3 mg l^{-1} thallium) are also included (Fig. 2A and B).

The dispersion characteristics are significantly modified as a result of microcolumn deposition/elution, the elution peak being relatively sharp (peak half-width of signal 3 S versus 9.4 S for direct injection) and intense (Fig. 2C), indicating a degree of preconcentration. Furthermore, the relatively sharp elution peak is an indication of fast exchange kinetic for the elution process. On the basis of consideration of peak height of conventional nebulization and peak height of sequential injection with a microcolumn, a dispersion coefficient ($16/26$) of 0.62 was calculated, even though the same volume ($500 \mu\text{l}$) of solution (3 mg l^{-1} thallium) was used in the deposition/elution step. Comparison of the area of the signals of microcolumn elution peak (Fig. 2C) and direct injection (Fig. 2B) indicate that a recovery of more than 98% is obtained with a single injection of eluent.

3.1. Effect of physical and chemical parameters

As shown in previous studies concerned with modified alumina, microcolumn pre-concentration [37–39], the deposition/elution processes are influenced by FI parameters, such as carrier stream flow rate, nature and flow rate of eluent, sample pH, column length, etc. These variables were, therefore, critically studied to maximize recovery of thallium.

PH of the solution have important role in deposition and recovery of trace amount of analyte in FI preconcentration system. As shown in (Fig. 3), when the pH of solution was varied from 2.5 to 11, the Tl(I) deposition was found to be independent of sample pH. This can be mention as an advantage of the system, as accurate control of the pH is not required. The pro-

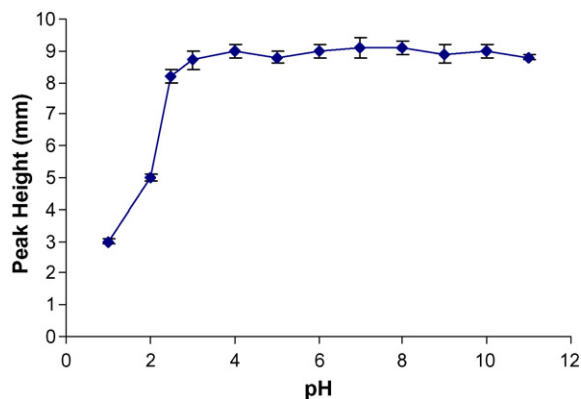


Fig. 3. Effect of pH on retention of thallium. Concentration: $50 \mu\text{g l}^{-1}$, concentrated volume: 10 ml, eluent: $500 \mu\text{l}$ of sodium thiosulfate (1 mol l^{-1}).

gressive decrease in retention of thallium at lower pH is due to protonation of oxine. However, for further work a pH of ~ 6 –7 was selected as it was more convince.

The choice of suitable eluent is very important in the design of an FI-on-line microcolumn preconcentration system to AAS. In order to obtain high enrichment factor, an eluent must have fast kinetic for quantitative desorption of the analytes and should not effect their accurate determination. The effectiveness of $500 \mu\text{l}$ of thiourea (1 mol l^{-1}), EDTA (0.01 mol l^{-1}) nitric acid (1.5 mol l^{-1}) and thiosulfate (1 mol l^{-1}) in eluting thallium (deposited from processing of 10 ml of 0.5 mg l^{-1} of Tl solution) from the microcolumn were compared. EDTA ($\sim 0\%$ recovery) and thiourea ($\sim 20\%$ recovery) were ineffective eluents. No differences in elution efficiency were detected for 1 mol l^{-1} sodium thiosulfate and 2 mol l^{-1} nitric acid. However, with nitric acid as eluent, some of the oxine was washed from the sorbent, and thus the reproducibility of the microcolumn was impaired; whereas, with thiosulfate the oxine was retained on the alumina, so it was adopted for further work. Elution of thallium was dependent on eluent concentration and at least 1 mol l^{-1} of sodium thiosulfate was required for effective elution (Fig. 4). At concentration less than 1 mol l^{-1} of eluent the elution was incomplete.

The efficiency of flow rate on analyte deposition on, microcolumn was considered by varying the flow rate from 1 to

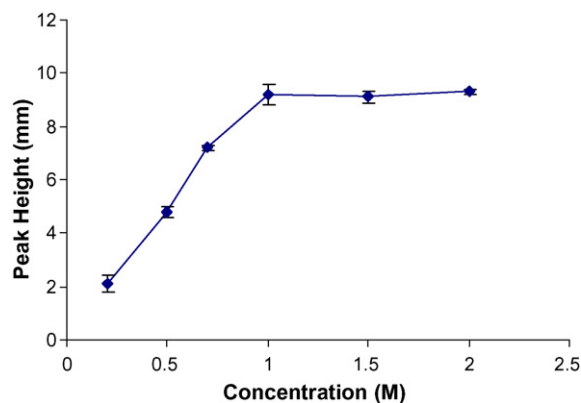


Fig. 4. Effect of eluent concentration on desorption of thallium(I). pH of solution: ~ 6 –7, concentration: $50 \mu\text{g l}^{-1}$, concentrated volume: 10 ml, eluent volume: $500 \mu\text{l}$.

Table 1
Determination of species of thallium in synthetic solution

Thallium concentrate Tl(I) + Tl(III) (mg l ⁻¹)	% recovery ^a	
	Tl(I)	Tl(III)
0.2 + 0.2	98.0 ± 0.5	99.4 ± 0.3
0.1 + 0.5	101.1 ± 0.1	98.0 ± 0.3
0.5 + 0.1	97.0 ± 0.4	99.3 ± 0.4
0.3 + 0.2	102.0 ± 0.6	100.0 ± 0.2
0.1 + 1.0	98.5 ± 0.3	99.7 ± 0.4
1.0 ± 0.1	101.5 ± 0.5	98.7 ± 0.2

Preconcentrated volume: 10 ml, flow rate: 3 ml min⁻¹, eluent: sodium thiosulfate (500 μl, 1 mol l⁻¹).

^a Mean and S.D. of three independent measurements.

5 ml min⁻¹, while keeping the amount of preconcentrated thallium constant at 5 μg. It was found that for a flow rate less than 3.5 ml min⁻¹ signal response was independent of flow rate. Use of higher flow rate, however, resulted in a sharp decrease in signal, suggesting impaired deposition efficiency as a consequence of short contact time. Subsequent sample loading was performed at a flow rate of 3 ml min⁻¹. When flow rate during elution was varied, a virtually linear increase in peak height response was observed that leveled off at a flow rate higher than the uptake of the nebulizer. This increase in peak height is due to starvation of the nebulizer at low flow rate. The elution flow rate was chosen to match the recommended sample uptake of the atomic absorption spectrometer (3 ml min⁻¹).

The effect of length of the column on efficiency of analyte deposition was considered and a 3 cm packed microcolumn was found to be sufficient.

3.2. Evaluation of sorbent properties

The breakthrough capacity of immobilized oxine microcolumn under the working conditions exceeded 812 μg of thallium(I) per gram of packing materials. This high value suggested high performance of microcolumn even in the presence of competing ions.

The capability of microcolumn for preconcentration of Tl⁺ and Tl³⁺ in the absence of hydroxylamine and EDTA, and at optimum pH and flow rate was considered by processing 5 ml of 0.20 mg l⁻¹ solution of either Tl⁺, Tl³⁺ or mixture of both. The results revealed that the column did not distinguish between different species of thallium. However, in the presence of EDTA, only thallium(I) was retained on the column. So, for determination of total thallium, Tl(III) was reduced to Tl(I) by hydroxylamine hydro chloride. Furthermore, the capability of sorbent in speciation of thallium was investigated by processing synthetic solution of mixture of Tl(I) and Tl(III) according to the given procedure. Results of Table 1 shows that the recovery of both species of thallium is quantitative, thus the system is capable of speciation of thallium. A signal micromicrocolumn was subjected to 10 loading and elution process, and was found that, retention of the sorbent did not change even after 10 cycles of sorption and desorption.

Table 2
Effect of sodium chloride salt concentration on recovery of thallium

Concentration (mol l ⁻¹)	% recovery
0.1	98.9 ± 1
0.5	101.0 ± 0.2
1.0	100.0 ± 0.1
1.5	100.0 ± 0.3
2	95.0 ± 2

Thallium concentration: 0.5 mg l⁻¹, preconcentrated volume: 10 ml, flow rate: 3 ml min⁻¹, eluent: sodium thiosulfate (500 μl, 1 mol l⁻¹).

3.3. Analytical performance

Twenty five and 50 ml of standard solutions were proceed (in triplicate) at a sampling flow rate of 3 ml min⁻¹, and the graph of absorbance (as peak height) versus thallium(I) concentration were linear over the range of 30–300 and 20–200 μg l⁻¹ of thallium, respectively. The equations of calibration graphs were $H = 0.0463C + 0.173$ and $H = 0.0886C + 0.0724$ (where H is the peak height and C is the concentration) with correlation coefficient of 0.9992 and 0.9990, respectively. The calibration slopes increased proportionally with increasing preconcentration volume. Which indicate the retention/elution efficiency of the process is constant (~100%).

A possible concern was whether high enrichment factors could be realized for natural waters and, particularly, salt-rich matrices such as sea water, where high concentration of salts might affect the active site and impair deposition of thallium. So 10 ml of 0.5 mg l⁻¹ of thallium solution containing different concentration of salt was processed with the FI system. The results of Table 2 revealed that high concentration of salt did not affect the signal, thus the system is capable of enrichment of thallium in high salt material.

Furthermore the sensitivity and utility of the method in the presence of various cations and anions was examined (Table 3). A relative error of less than 5% was considered to be within the

Table 3
Effect of diverse ions in determination of Tl(I)

Ions	Mole ratio, M/(Tl ⁺)	% recovery
Mg ²⁺	1000	102.0 ± 0.5
Na ⁺	1000	97.8 ± 0.2
Ca ²⁺	500	103.0 ± 0.5
K ⁺	1000	100.0 ± 0.1
Zn ²⁺	1000	98.0 ± 0.6
Pb ²⁺	1000	97.5 ± 0.4
Cu ²⁺	1000	101.2 ± 0.1
Co ²⁺	1000	96.0 ± 0.2
Ni ²⁺	1000	96.0 ± 0.5
Cd ²⁺	750	99.0 ± 1.0
Cs ⁺	1000	100.8 ± 0.1
Fe ³⁺	500	95.5 ± 0.3
Ag ⁺	750	97.8 ± 1.1
Cl ⁻	1000	98.0 ± 1.0
I ⁻	1000	99.0 ± 0.7
CO ₃ ²⁻	500	98.0 ± 0.5
SO ₃ ²⁻	1000	97.4 ± 0.3

Thallium concentration: 0.5 mg l⁻¹, preconcentrated volume: 10 ml, flow rate: 3 ml min⁻¹, eluent: sodium thiosulfate (500 μl, 1 mol l⁻¹).

Table 4
Determination of thallium in real samples

Sample	Added	Found	% Recovery	GF-AAS
Tap water	–	ND ^a	–	0.4 ± 0.2 μg l ⁻¹
	20 μg l ⁻¹	20.4 ± 0.6 μg l ⁻¹	102.0 ± 0.9	–
Well water	–	ND ^a	–	1.0 ± 0.1 μg l ⁻¹
	30 μg l ⁻¹	30.2 ± 0.1 μg l ⁻¹	100.6 ± 0.5	–
Spring water	–	ND ^a	–	ND ^a
	25 μg l ⁻¹	24.9 ± 0.1 μg l ⁻¹	99.6 ± 0.3	–
Waste water	–	ND ^a	–	2.9 ± 0.3 μg l ⁻¹
	30 μg l ⁻¹	31.1 ± 0.5 μg l ⁻¹	103.6 ± 0.7	–
Hair	–	0.05 ± 0.02 μg g ⁻¹	–	0.05 ± 0.01 μg g ⁻¹
	0.05 μg g ⁻¹	0.11 ± 0.01 μg g ⁻¹	100.2 ± 1.0	–
Nail	–	0.14 ± 0.03 μg g ⁻¹	–	0.13 ± 0.05 μg g ⁻¹
	0.2 μg g ⁻¹	0.33 ± 0.05 μg g ⁻¹	95.0 ± 0.6	–
Coal	–	0.54 ± 0.01 μg g ⁻¹	–	0.55 ± 0.03 μg g ⁻¹
	1.0 μg g ⁻¹	1.50 ± 0.05 μg g ⁻¹	96.0 ± 0.5	–

Concentrated volume: 25 ml, flow rate: 3 ml min⁻¹, eluent: sodium thiosulfate (500 μl, 1 mol l⁻¹). ND: not detected.

^a Mean and S.D. of three determinations.

range of experiment error. In the presence of EDTA at the given level no significant interference was observed in the determination of thallium. Thus, the interference-free determination level of present system indicates that high concentration of matrix salts, have minimal effect on thallium species relative to matrix ions.

The relative standard deviation of 10 replicate measurements of 30 μg l⁻¹ thallium (I) with a sample volume of 25 ml was ±2.6%, the limit of detection based on three times the standard deviation of the blank signal with a sample volume of 25 ml was found to be 2.5 μg l⁻¹ of thallium.

In order to quantify thallium at low level (mg l⁻¹), the preconcentration capability of the FI system were investigated. Based on matching the slopes of calibration graph of FI system, and steady-state of conventional nebulization, a concentration factor of 77 and 147 for sampling volume of 25 and 50 ml were obtained respectively.

To assess the applicability of the proposed method to real samples, the procedure was applied to water (tap, well and spring water), waste water (taken from Koushk industry), hair, nail and coal samples, with diverse matrix cation and anion concentration. The results are given in Table 4. Reliability was checked by spiking experiment and comparing the results with data obtained by furnace atomic absorption analysis. The results show that in all samples, the thallium recovery is almost quantitative (from 95 to 100.2) and at 95% confidence limit, there is good agreement between the results of proposed method and furnace atomic absorption. Thus the FI–AAS procedure is suitable for the sample type examined.

The procedure was also applied to determination of thallium in two different certified reference alloys, BCR No. 288 and CRM 5406-90, with thallium concentration of 2.3 ± 0.1 and 45.8 μg g⁻¹, respectively. The amount of thallium in BCR and CRM were found to be 2.31 ± 0.09 and 45.7 ± 0.05 μg g⁻¹, respectively. These were in agreement with the certified val-

ues, indicating the suitability of the method for this type of alloys.

Furthermore to evaluate the validity of the proposed method for speciation of thallium, the recovery of different amount of Tl(I) and Tl(III) ions added to water samples taken from the river was carried out by the proposed method. The results indicate that the recovery of both species of thallium at all three levels tested is almost quantitative. Thus, the procedure is reliable for determination of thallium in a wide range of samples, and its speciation in water sample.

4. Conclusion

The proposed FI–FAAS procedure based on microcolumn of immobilized oxine provide a simple, sensitive and economical method for separation, preconcentration and speciation of thallium by flame atomic absorption spectrometry. The main advantage of the method are: ease and simplicity of preparation of microcolumn, high selectivity and reproducibility for separation, speciation, concentration and determination of thallium ions. With 25 ml preconcentration volume, more than seven samples can be analyzed in 1 h. The method can be successfully applied to determination of thallium in a wide range of real samples.

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