



# L-Tyrosine immobilized on multiwalled carbon nanotubes: A new substrate for thallium separation and speciation using stabilized temperature platform furnace-electrothermal atomic absorption spectrometry

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## ABSTRACT

An approach for the separation and determination of inorganic thallium species is described. A new sorbent, L-tyrosine-carbon nanotubes (L-tyr-CNTs), was used and applied to the analysis of tap water samples. At pH 5.0, L-tyr was selective only towards Tl(III), while total thallium was determined directly by stabilized temperature platform furnace-electrothermal atomic absorption spectrometry (STPF-ETAAS). The Tl(III) specie, which was retained by L-tyrosine, was quantitatively eluted from the column with 10% of nitric acid. An on-line breakthrough curve was used to determine the column capacity, which resulted to be 9.00  $\mu\text{mol}$  of Tl(III)  $\text{g}^{-1}$  of L-tyr-CNTs with a molar ratio of 0.14 (moles of Tl bound to moles of L-tyr at pH 5). Transient peak areas revealed that Tl stripping from the column occurred instantaneously. Effects of sample flow rate, concentration and flow rate of the eluent, and interfering ions on the recovery of the analyte were systematically investigated. The detection limit for the determination of total thallium ( $3\sigma$ ) by STPF-ETAAS was 150  $\text{ng L}^{-1}$ . The detection limit ( $3\sigma$ ) for Tl(III) employing the separation system was 3  $\text{ng L}^{-1}$ , with an enrichment factor of 40. The precision of the method expressed as the relative standard deviation (RSD) resulted to be 3.4%. The proposed method was applied to the speciation and determination of inorganic thallium in tap water samples. The found concentrations were in the range of 0.88–0.91  $\mu\text{g L}^{-1}$  of Tl(III), and 3.69–3.91  $\mu\text{g L}^{-1}$  of total thallium.

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## 1. Introduction

Thallium is a metal of great toxicological concern and its prevalence in the natural environment has steadily increased as a result of manufacturing and combustion practices, such as electronics, pharmaceuticals, alloys, and glass manufacture. 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 [1].

Thallium can be found in nature as Tl(I) and Tl(III) ions. Each redox state of the element exhibits different bioavailability and

toxicity properties [2]. The toxicological properties of inorganic Tl species differ widely. Tl(III) is approximately 50,000 times more toxic than Tl(I) and, in comparison with other elements, Tl(III) is 43,000 times more toxic than Cd on a free-ion basis [3]. From a toxicological and an environmental point of view, the analytical speciation and determination of the content of Tl in biological and environmental matrices are unsatisfactory. Consequently, studies should be focused on these aspects [4,5].

Sensitive and accurate methods for Tl determination are increasingly in demand as a consequence of the intense toxic properties displayed by the metal. Electrothermal atomic absorption spectrometry (ETAAS) appears to be the methodology of choice for Tl determination at very low concentrations [4]. This very sensitive and relatively simple technique has been used by several researchers for thallium determination [6–9]. However, the direct determination of thallium by ETAAS involves many difficulties because of spectral and non-spectral interferences in environmental matrices [10–12]. Interferences may be overcome to various degrees by applying the “stabilized temperature platform furnace” (STPF) concept.

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From the scenario described above, it can be concluded that the level of an element is not sufficient to evaluate its impact on the environment, its bioavailability, and its toxicity. This fact has stimulated the development of species-selective analytical methodologies during the last decade [13]. In this sense, solid phase extraction (SPE) appears as an effective analytical approach, demonstrating selectivity for the elements determined. In addition, SPE can also extend the detection limits and solve problems referred to matrix interferences [14–16].

Amino acids and peptides have shown growing interest as new substrates for SPE and metal speciation analysis due to their metal binding capacity. This type of research includes advances in different fields such as nanotechnology [17], metal remediation [18–20], preconcentration and separation [21]. Amino acids exhibit diverse functional groups with different metal binding capacities. In general, they act as bidentate ligands with coordination involving the carboxyl oxygen and the nitrogen atom of the amino group [22]. Selectivity, strong binding capacity, and environmental innocuousness [23–26] are some of the properties that amino acids have turning them into ideal molecules for trace element preconcentration and monitoring in environmental matrices.

The immobilization possibility of amino acids into solid supports provides the opportunity of column packing [20]. Currently, carbon nanotubes (CNTs) have been proposed as a novel solid phase extractants for various inorganic and organic compounds/elements at trace levels [27–29]. The hexagonal arrays of carbon atoms in graphite sheets of CNTs surface are ideal for strong interactions with other molecules. The high specific surface of CNTs enhances the number of immobilized molecules, providing a higher metal retention with easy release and reusability [30–32]. Under these conditions, amino acids acquire a specific binding orientation in the presence of a complexing metal. These columns inserted into on-line systems can be used for analytes retention and speciation.

In this study, the retention of inorganic thallium species using L-tyr immobilized onto CNTs was evaluated. Tl(III) was selectively retained by a simple pH adjustment. Other analytical parameters, such as sample flow rate, eluent concentration, eluent flow rate, and eluent volume, were also evaluated. In addition, breakthrough curves and eluent profile were analyzed. STPF-ETAAS was employed for total Tl detection. L-Tyr-CNTs was employed for Tl(III) separation and speciation. The retention system was successfully applied to the speciation analysis of inorganic thallium in tap water samples. To the best of our knowledge, this is the first time that L-tyr immobilized on CNTs has been applied to the speciation of thallium.

## 2. Experimental

### 2.1. Instrumentation

The determination of thallium concentrations was carried out on a Shimadzu Model AA-6800 atomic absorption spectrometer (Tokyo, Japan) equipped with a background correction system employing a continuum source, a GFA-EX7 electrother-

mal atomizer, and an ASC-6100 autosampler. L'vov graphite tubes (Shimadzu, Tokyo, Japan) were used in all experiments. A thallium hollow-cathode lamp (Hamamatsu, Photonics K. K., Japan) was employed as radiation source operated at 6 mA, the analytical wavelength of 276.8 nm was employed for all measurements. The ETAAS instrumental and operating conditions are listed in Table 1.

For breakthrough curves and eluent profile analysis the same equipment was employed, but in the air/acetylene flame mode. A Gilson Minipulse peristaltic pump (Villiers, Le-Bell, France) and Tygon type-pump tubes (Ismatec, Cole-Parmer Instrument Company, Niles, IL, USA) were employed to propel sample and eluent.

A conical minicolumn (40 mm length, 4.5 mm internal upper-diameter, and 1.5 mm internal lower diameter) was used as sorbent holder. The conical minicolumn was prepared by placing 10 mg of L-tyrosine-CNTs into an empty conical tip using the dry packing method. To avoid filling losses when the sample solution passed through the conical minicolumn, a small amount of quartz wool was placed at both ends.

### 2.2. Reagents

Unless otherwise stated, the chemicals used were of analytical reagent grade and, therefore, no further purification was required. A 1000 mg L<sup>-1</sup> Tl(I) stock standard solution was prepared by dissolving 1.2349 g of thalious sulphate (BDH, England) in ultrapure water up to 1000 mL. Thallium (III) was obtained by oxidation of thallium (I) after adding a few drops of bromine water, warmed to remove excess of bromine, and cooled [33].

Commercial multiwalled CNTs were obtained from Sunnano (Jiangxi, China). L-Tyrosine was obtained from MP Biomedicals Inc. (Chicago, IL, USA).

Chemical modifier solutions (100 mL of a concentration of 10,000 mg L<sup>-1</sup>) were prepared by dissolution of the proper solid salt into deionized water as follows: for phosphate chemical modifier, 1.3905 g of diammonium hydrogen phosphate (Merck, Darmstadt, Germany) were weighted and diluted; for magnesium chemical modifier, 10.5495 g of Mg(NO<sub>3</sub>)<sub>2</sub>·6H<sub>2</sub>O (Merck, Darmstadt, Germany) were weighted and diluted; and for palladium chemical modifier, 2.16 g of palladium nitrate (Merck, Darmstadt, Germany) were weighted and diluted.

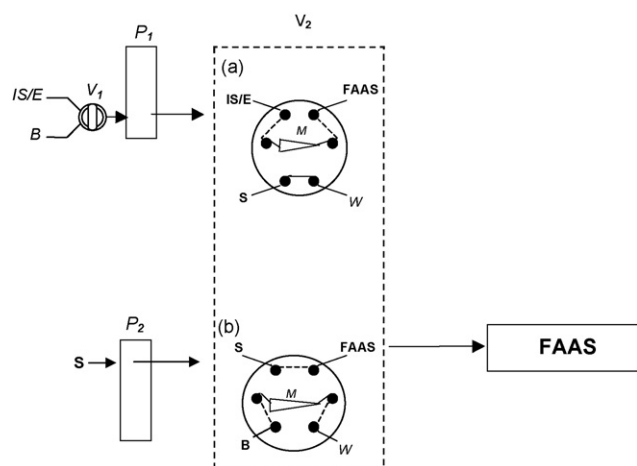
### 2.3. Immobilization procedure

About 10 mg of commercial multiwalled CNTs were treated with concentrated nitric acid to clean them and eliminate possible Fe residues present in CNTs due to the generation process. This procedure also allowed the generation of –COOH and –OH groups on the CNTs surface, improving their solubility [34]. After this, CNTs were centrifuged, filtrated, and dried.

The resultant powder was suspended in phosphate buffer solution, pH 7.0. An aliquot of 10 mg of the amino acid L-tyrosine was added to this buffer solution. After this, the solution was heated for 48 h at 45 °C. Finally, it was filtered and the CNTs were dried at room temperature.

**Table 1**  
Graphite furnace temperature program for Tl determination.

Step	Temperature (°C)	Ramp time (s)	Hold time (s)	Ar flow (mL min <sup>-1</sup> )
Drying (I)	120	20	–	0
Drying (II)	250	10	–	250
Pyrolysis (I)	800	10	10	250
Pyrolysis (II)	800	–	2	0
Atomization	1600	–	3	0
Cleaning	2000	–	1	250



**Fig. 1.** Schematic diagram of the instrumental setup employed for metal binding studies. IS, influent solution; B, buffer; S, standard; E, eluent; W, waste; V<sub>1</sub>, valve 1; V<sub>2</sub>, valve 2; P<sub>1</sub>, pump 1; P<sub>2</sub>, pump 2 M, minicolumn filled with L-tyr-CNTs.

## 2.4. Sample collection and pre-treatment

Water samples were filtered through a 0.45 mm pore size membrane filter in order to eliminate suspended particulate matter and were stored at 6 °C until analysis. Before Tl(III) analysis, aliquots of 10 mL of each sample were adjusted to the working pH value with small amounts of HNO<sub>3</sub> and NaOH. Total Tl content was determined directly by ETAAS.

## 2.5. Metal binding studies

### 2.5.1. Procedure

The uptake and release of Tl by L-tyr immobilized on CNTs were studied using an on line-FAAS procedure (Fig. 1). Before starting the experiments, a cleaning step of 5 min with 10% of HNO<sub>3</sub> was performed. After that, a pH 5 nitric solution (buffer, B) was pumped (pump 1, valve 1 in position B) through the column for 2 min at 1 mL min<sup>-1</sup> to recondition the column to the retention pH. A 10 mg L<sup>-1</sup> Tl(III) solution (influent solution, IS, valve V<sub>1</sub> in position IS/E) was then passed through the column at a flow rate of 1 mL min<sup>-1</sup>. The end of the column was connected to the FAAS instrument and the Tl signal was monitored (valve V<sub>2</sub> in position a). Once the effluent concentration reached the influent concentration, the sample flow was stopped. This stage was performed in order to obtain the Tl(III) breakthrough curve at pH 5. Pump 2 was employed to obtain lectures from the standards, valve 2 in position with pump b.

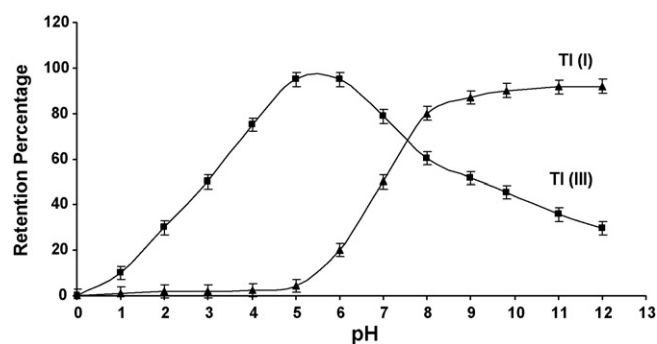
After that, Tl was eluted from the column with a 10% HNO<sub>3</sub> solution (eluent, E). It was verified that acids can cause a reversible change in the tertiary structure of amino acids providing efficient and rapid release of metals from the binding cavity [35]. Other eluents such as hydrochloric acid were tested and no significant differences were obtained. Finally, the column was reconditioned and the process started again.

An Origin® 7.0 program was used to perform calculations related to the amount of metal bound to the column from the breakthrough curves.

## 2.6. Analytical performance studies

### 2.6.1. Preconcentration procedure

Analytical performance studies were carried out employing ETAAS as the detection system. The STPF-ETAAS instrumental and operating conditions are listed in Table 1. The furnace program and chemical modifiers were chosen according to those reported by



**Fig. 2.** Dependence of thallium (I and III) retention on pH of loading solutions. Volume of sample: 10 mL; Tl(I) and Tl(III) concentrations: 0.1 µg L<sup>-1</sup>; HNO<sub>3</sub> concentration: 10.0% (v/v).

Butcher and Sneddon [36]. The chemical modifiers employed were 1000 mg L<sup>-1</sup> solutions of Pd, Mg, and phosphate.

The procedure employed in this FI-STPF-ETAAS system involved the same column cleaning, conditioning, and eluting steps mentioned in Section 2.5.1. However, in this case, different volumes of a 0.1 µg L<sup>-1</sup> Tl(III) solution were passed through the column and then eluted. Finally, 20 µL of the eluate were analyzed employing 10 µL of modifiers, reaching a final volume of 30 µL to be injected into the graphite furnace tube.

Total Tl concentration was determined directly by STPF-ETAAS. Samples and standards were analyzed under the same conditions. The operation conditions were established and the determinations were carried out.

## 3. Results and discussion

### 3.1. pH studies

In order to optimize the sorption conditions for Tl retention on L-tyr-CNTs, the Tl signal intensity (peak areas) was monitored by STPF-ETAAS as a function of the solution pH that passed through the conical minicolumn. It has been reported [35] that pH is a very important factor for the adsorption process of metals on amino acids. This process is related to the protonation and the deprotonation of the amino acids and the metal specie present in solution [35]. Fig. 2 shows that optimal pH values for Tl(I) retention, which were in the range of 8.0–12.0. Tl(III) was also retained at these pH values, but with recoveries of 50% approximately. The retention of Tl(III) showed a maximum in the range of pH between 4.5 and 5.5 reaching recoveries as higher as 98%. Tl(I) was not retained at these pH values. As a result, pH 5.0 was used in order to achieve the best conditions for Tl speciation analysis. At this pH value, Tl<sup>3+</sup> is the main specie present in solution that can be interacting with the sorbent [37].

### 3.2. Determination of column capacity

The column capacity of the L-tyr-CNTs system for Tl(III) retention at pH 5 was assessed through an on-line procedure with a thallium influent solution of 10 mg L<sup>-1</sup> at a flow rate of 1 mL min<sup>-1</sup>. FAAS was employed as detection system. The total amount of Tl(III) bound to L-tyr-CNTs at pH 5.0 was 9.00 µmol g<sup>-1</sup>, which was determined by integration of the breakthrough curve shown in Fig. 3.

The sorbent employed in this study is the same that the one previously used for Co separation [38]. Therefore, it can be concluded that the sorbent shows an appropriate stability and reusability. In addition, the amount of immobilized amino acid was determined in the mentioned work [38], corresponding to 600 mg L-tyr g<sup>-1</sup> CNTs (equivalent to 3173 µmol of L-tyr g<sup>-1</sup> CNTs). From this value, a cal-

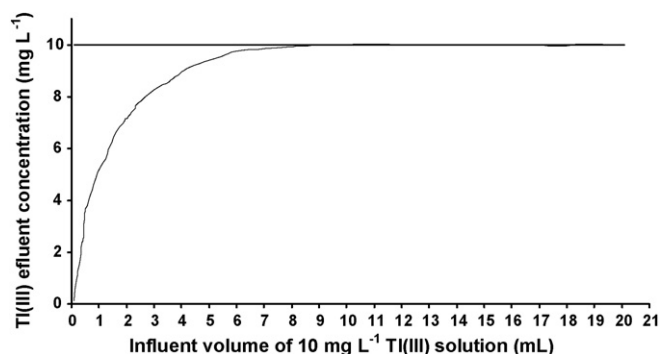


Fig. 3. Breakthrough curves of L-tyr-CNTs for 10 mg of  $\text{Tl(III)}$  solution (pH 5.0) loaded at a flow rate of  $1.0 \text{ mL min}^{-1}$ .

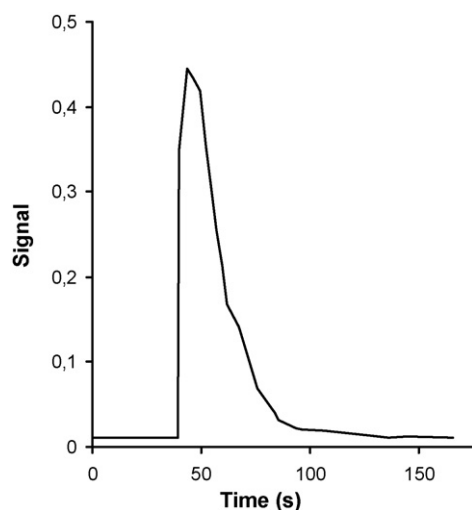


Fig. 4. Transient absorbance signal observed when on-line Tl stripping with 10%  $\text{HNO}_3$  was carried out.

culus of the molar ratio (moles of Tl bound per mol of L-tyr at pH 5) can be performed, which turned to be equal to 0.14.

### 3.3. Elution profile

It has been proposed that the elution of metals from retained amino acids onto solid substrates in the presence of acids occurs fast and instantaneously with high recoveries [35]. The elution profile is an interesting analytical tool to analyze the Tl elution's behavior from L-tyr-CNTs. Fig. 4 shows the time-dependent, transient signal obtained from stripping the metal from the column. The column was previously loaded until saturation. The peak shape shows the same behavior described for other amino acids immobilized on solid supports [35]. The elution step is a fast and instantaneous kinetics desorption process. The transient signals for a complete metal removal lasted less than 40 s, which corresponds to 0.6 mL of a 10%  $\text{HNO}_3$  solution. The trailing edges of the strip peaks shows a very straighten increase, with very low dispersion, followed by a

slightly decay of the signal with a “tale” at the end of the strip, describing a very acute peak. The straighten increase could be attributed to accessible binding sites of the sorbent to the eluent allowing a fast proton exchange. On the other hand, the slightly decay could be attributed to certain regions of the CNTs with unfavorable access to the eluent.

### 3.4. Parameters affecting Tl(III) preconcentration

Parameters affecting Tl(III) preconcentration were evaluated employing STPF-ETAAS as the detection system. The analytical parameters studied were the following.

#### 3.4.1. Influent flow rate

The sample flow rate through the column packed with CNTs is a very important parameter to optimize, since this is one of the steps that control the time of analysis [39]. We could verify that with flow rates up to  $5.0 \text{ mL min}^{-1}$  there was no effect on the analyte recovery, which resulted to be between 98 and 100%. Higher flow rates were avoided because the recovery decreased and the back pressure generated could damage the FI system.

#### 3.4.2. Eluent

Nitric acid was chosen as eluent. This acid has a dual function: first, a quantitative release of the bound metal [19–21]; and second,  $\text{HNO}_3$  stabilizes the Tl signal, preventing chloride interferences during Tl determination [40]. An enhancement of Tl signal was observed as the concentration of nitric acid increased up to 10% (v/v). No further Tl signal improvement was observed beyond this nitric acid concentration. As a result, an eluent concentration of 10% (v/v) was used for further experiments.

#### 3.4.3. Elution flow rate

It was verified that flow rates up to  $5.0 \text{ mL min}^{-1}$  were well tolerated by the column. As mentioned previously, higher flow rates were avoided because the recovery decreased and the back pressure generated could damage the FI system.

### 3.5. Analytical performance

The analytical performance of the proposed system was studied by loading 20 mL of a  $0.1 \mu\text{g L}^{-1}$  Tl(III) solution on the column. The limit of detection (LoD), expressed as the amount of Tl that produced a net signal equal to three times the standard deviation ( $3\sigma$ ) of 10 replicate lectures ( $n=10$ ) of a blank solution, was equal to  $3 \text{ ng L}^{-1}$ . The calibration graph using the proposed preconcentration system was linear with a correlation coefficient of 0.9991 from concentrations close to the detection limit up to, at least,  $2 \mu\text{g L}^{-1}$ . The precision, expressed as the relative standard deviation (RSD), for five replicate determinations of a  $1 \mu\text{g L}^{-1}$  of Tl solution was 3.4%. An enrichment factor of 40 was obtained when 20 mL of Tl solution were eluted with 0.5 mL of a 10% (v/v)  $\text{HNO}_3$  solution. Table 2 compares the analytical performance of this proposed method with others reported for Tl determination. This methodology showed a comparable analytical performance with other studies that also used the same detection system.

Table 2

Procedures reported in the literature for preconcentration and determination of thallium.

Detection limit ( $\text{ng L}^{-1}$ )	Enrichment/enhancement factor	Sample volume (mL)	Technique	Speciation analysis	Reference
12	40	20	ETAAS	Yes	This work
2500	77	25	FAAS	Yes	[4]
0.025	125	–	ICP-MS	Yes	[5]
50	45	5	ETAAS	No	[6]
2000	55	–	FAAS	Yes	[41]



**Table 3**Recovery study for Tl and Tl(III) determination (95% confidence interval,  $n = 6$ ).

Aliquot	Base value ( $\mu\text{g L}^{-1}$ )	Tl added ( $\mu\text{g L}^{-1}$ )	Tl(III) added ( $\mu\text{g L}^{-1}$ )	Tl found ( $\mu\text{g L}^{-1}$ )	Recovery (%) <sup>a</sup>
1 <sup>b</sup>	0.9	–	–	$0.98 \pm 0.03$	–
2 <sup>b</sup>	0.9	–	0.1	$1.00 \pm 0.02$	100
3 <sup>b</sup>	0.9	–	0.5	$1.39 \pm 0.03$	98
4 <sup>b</sup>	0.9	–	1	$1.93 \pm 0.05$	103
5 <sup>b</sup>	0.9	–	2	$2.87 \pm 0.04$	98.5
6 <sup>c</sup>	3.8	–	–	$3.78 \pm 0.06$	–
7 <sup>c</sup>	3.8	1	–	$4.86 \pm 0.06$	106
8 <sup>c</sup>	3.8	2	–	$5.82 \pm 0.07$	101
9 <sup>c</sup>	3.8	5	–	$8.81 \pm 0.2$	100.2

<sup>a</sup>  $100 [( \text{found} - \text{base} ) / \text{added}]$ .<sup>b</sup> Recovery of Tl(III).<sup>c</sup> Recovery of total Tl.

### 3.6. Interference studies

The effects of potential interference species at the concentration levels at which they may occur in the studied sample were tested. For this purpose, synthetic Tl solutions were prepared and the signal was monitored. The presence of cations such as  $\text{Na}^+$ ,  $\text{K}^+$ ,  $\text{Ca}^{2+}$  were tolerated up to at least  $1000 \text{ mg L}^{-1}$ . On the other hand, the effects of anions such as  $\text{CO}_3^{2-}$ ,  $\text{SO}_4^{2-}$ ,  $\text{Cl}^-$  and  $\text{NO}_3^-$  were tolerated up to at least  $1000 \text{ mg L}^{-1}$ . The major ions present in tap water did not interfere with the preconcentration of Tl(III) and the tolerable limits of the mentioned interferences are high enough to allow the tap water analysis.

### 3.7. Validation study

Unfortunately, there are no standard reference materials with a certified content of individual species of Tl. For these cases, a recovery study can be considered as a validation alternative. The content of Tl(III) in tap water was determined through the SPE system using L-tyr-CNTs. The total Tl content was determined directly by STPF-ETAAS. Despite the fact that recovery studies should be avoided because they may disregard the nature of the chemical species in which the element is present, they are an alternative to estimate at least the accuracy.

Tap water was divided in portions of 5 mL each. The proposed method was applied to six portions (three for total Tl and three for Tl(III)) and the mean Tl concentration of each specie was taken as a base value. Then, increasing quantities of Tl and Tl(III) were added to the other aliquots and the same procedure was followed. Since the sensitivity of the calibration plots of Tl(I) and Tl(III) employing STPF-ETAAS was indistinct, the recovery study for total Tl was carried out by spiking the samples with Tl(III). The recovery values were between 98% and 103% for Tl(III) and 100.2–106% for total Tl (Table 3). The results were compared with the  $t$ -test and no significant differences were observed at 95% confidence level. The recovery studies for the other samples showed similar performance.

### 3.8. Application to real samples

The method was applied to the determination of inorganic thallium in tap water. The found concentrations were in the range of  $0.95\text{--}1.01 \mu\text{g L}^{-1}$  of Tl(III), and  $3.69\text{--}3.91 \mu\text{g L}^{-1}$  of total thallium content. These results were obtained by applying the standard addition method and are shown in Table 3. These found thallium concentrations are in good agreement with those obtained by Chamsaz et al. [42]. However, these thallium levels are slightly higher than the maximum contaminant level (MCL) established by the U.S. Environmental Protection Agency of  $2 \mu\text{g L}^{-1}$  for tap water [43].

## 4. Conclusion

This study supports that L-tyrosine immobilized on multiwalled CNTs is an appropriate sorbent for the retention of thallium, allowing its preconcentration and speciation. The proposed system provided an accurate and precise alternative for the selective determination of Tl(III) at  $\text{ng L}^{-1}$  levels with quantitative recoveries. In addition, the total Tl content was properly and directly determined by STPF-ETAAS. The method is simple and no masking agents were necessary.

The analytical performance of the method showed an acceptable enrichment factor with an adequate detection capability to comply with the analyte concentration levels usually expected in real samples.

The chosen amino acid combined with the high CNTs specific surface demonstrated an excellent retention capacity towards Tl. This study confirmed the selectivity that amino acids present towards specific species of an element and their suitability for speciation analysis. Further research is needed to fully explore the analytical capabilities for elemental speciation using different amino acids, and their application to pharmaceutical, biological, and environmental samples.

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