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Speciation analysis of thallium using electrothermal AAS following on-line pre-concentration in a microcolumn filled with multiwalled carbon nanotubes

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Abstract The enrichment ability of carbon nanotubes (CNTs) was investigated and a new method established for the determination of trace thallium species in environmental samples using electrothermal atomization-atomic absorption spectrometry (ETAAS). The CNTs were employed as sorbent substrate in a continuous flow system coupled to ETAAS. Parameters influencing the recoveries of thallium were optimized. Under optimal conditions, the detection limit and precision of the method were 0.009 μg L^{-1} and 3.9%, respectively. The method was applied to the determination of thallium in real environmental samples and the recoveries were in the range from 96 to 100%. This system was able to separate thallium (I) from the matrix, which allowed its selective determination. The total thallium content was then determined by reducing Tl(III) with hydroxylamine. All these experimental results indicated that this new procedure can be applied to the determination of trace thallium in drinking water samples.

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Introduction

Thallium is a trace element which occurs in small amounts in sulfur-containing ores and potassium minerals. The occurrence of this element is mainly caused by ore smelting, handling and processing of waste products from the metallurgic industry, resulting in thallium emissions [1]. Tl is a cumulative poison of high toxicity, and lacks taste, smell or other warning attributes. Because of the properties of this element, its compounds (e.g. Tl_2SO_4) are used for the control of rodents under restricted conditions. In human beings, poisoning from toxicological exposure to thallium happened in case of homicide, suicide and inadvertence [2]. 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 state of the element exhibits different bioavailability and toxicity properties [3, 4]. For this reason, studies not only attempt to determine Tl total concentration, Tl species determination is also important as well [3–5]. Regarding the toxicity of this metal, its presence, even in small concentrations in natural waters that serve for drinking or irrigation, might be a certain signal of mixing pure water with contaminated wastewater [6].

Owing to their high sensitivity and selectivity, atomic absorption spectrometric and particularly electrothermal atomic absorption spectrometric (ETAAS) methods are widely used for thallium determination in environmental samples [7, 8]. However, direct Tl determination by

ETAAS involves many difficulties because of spectral and non spectral interference in environmental matrices [9–13]. While many matrix interferences may be overcame by applying the "stabilized-temperature platform furnace" (STPF) concept together with matrix modification [9, 10, 12, 14]; undoubtedly, matrix separation is often necessary to avoid spectral and non-spectral effects. Other alternative is an ETAAS determination of thallium preceded by separation and pre-concentration [13–22]. As an alternative of the classical batch procedures, a flow injection (FI) solid phase separation and pre-concentration coupled to ETAAS is an interesting way of trace determination [23, 24].

Carbon nanotubes (CNTs) have been exploited in many fields such as biosensors [25, 26], modified electrodes [27, 28], field-effect transistors [29] among others, based on their peculiar structural characteristics [30, 31]. Because CNTs have a large specific surface area, they possess excellent adsorption ability [32]. In a previous report [33] we have employed CNTs placed in a compacted microcolumn for the pre-concentration of V species, followed by ETAAS determination. This on-line coupling with STPF-ETAAS is a promising alternative due to the low-sample consumption, simplicity, high selectivity and sensitivity, for species-specific ultra-trace elemental determination.

This work proposes a new application of CNTs. They were included as sorbent into an on-line pre-concentration manifold to determine thallium species at trace levels in drinking waters in conjunction with STPF-ETAAS. The only pH adjustment was enough for Tl(I) retention, whilst Tl(III) was not retained on CNTs. The retention system was successfully applied to inorganic thallium speciation in tap water. To the best of our knowledge this is the first time that CNTs is employed for thallium speciation.

Experimental

Reagents

Ultra-pure water (18 MΩ cm) was an EASY pure RF obtained from Barnsted (Iowa, USA) (http://www.barnsteadthermolyne.com). All reagents were of analytical-reagent grade and the presence of thallium was not detected within the working range.

A 1,000 mg L^{-1} Tl(I) stock standard solution was prepared by dissolving 1.2349 g of thallium (I) sulphate (AnalaR, BDH) (http://www.bdhme.com) in 1,000 ml of ultrapure water. Tl(III) was obtained by oxidation of thallium (I) by adding a few drops of bromine water, warmed to remove excess of bromine and cooled.

Sample collection and pre-treatment

Water samples were from commercial drinking water obtained locally. After analysis, all samples were filtered through a 0.45 μm pore size membrane filter in order to eliminate suspended particulate matter and were stored at 6 °C. Before Tl(I) determination, 10 ml of each sample were adjusted to the working pH with small amounts of HNO_3.

In order to determine the total thallium content, it was necessary to reduce Tl(III) to Tl(I) prior to its sorption on CNTs. This was made by adding 0.1 mol L^{-1} hydroxylamine solution.

Apparatus

The measurements were performed with a Shimadzu Model AA-6800 atomic absorption spectrometer (Tokyo, Japan) (http://www.shimadzu.com), equipped with a GFA-EX7 atomizer and an ASC-6100 autosampler. Integrated platform (L'vov) graphite tubes, Shimadzu (Tokyo, Japan), were used in all experiments. A thallium hollow-cathode lamp, Hamamatsu, Photonics (K.K., Japan) (http://www.hamamatsu.com), was employed as radiation source operated at 6 mA. The 276.8 nm analytical line was employed in all determinations. A Minipuls peristaltic pump, Gilson (Villiers-Le-Bel, France) (http://www.gilson.com), was used. Sample injection was achieved using a Rheodyne Model 50 4-way (Cotati, CA, USA) (http://www.rheodyne.com). A conical mini-column (an empty micropipette tip) was used as the CNTs holder. Tygon pump tubing, Ismatec, Cole-Parmer Instrument Company (Niles, IL, USA) (http://coleparmer.com), was employed to propel the sample and reagents.

Nanotubes preparation

Purified multi-walled carbon nanotubes (MWNTs-3100) from Nanocyl (http://www.nanocyl.com) were employed. The MWCNTs were treated as it has been described elsewhere [33]. Previous to the treatment, the nanotubes were sonicated in ethanol in the proportion of 15 mg MWNT in 500 mL of ethanol for 30 min to separate the agglomerates and to be able to treat each MWNT in the same way. Then, the mixture was filtered through a 0.45 mm Millipore nylon filter membrane and the resulting MWNT were dried overnight in a vacuum oven at 120 °C.

Column and sample preparation

The conical mini-column was prepared by placing an adequate mass of carbon nanotubes into an empty conical-tip using the dry packing method. Here, the CNTs filled a volume equivalent to 10 µL when the empty tip was filled with water.

To avoid loss of CNTs when the sample solution passed through the conical mini-column, a small amount of quartz wool was placed at each end of the conical micro-column. The column was then mounted on the furnace autosampler to form the pre-concentration system. Prior to use, a nitric acid solution (7.0 mol L^{-1}) was passed through the CNTs micro-column. After that, the column was washed with ultra-pure water until neutral pH. The water samples were filtered through 0.45 µm pore size membrane filters immediately after sampling, and were adjusted to pH 4.0 with an adequate amount of HNO_3 solution immediately before use.

Pre-concentration procedure and determination

In Fig. 1 it is shown a schematic diagram of the experimental setup. Before loading, the conical micro-column was conditioned for pre-concentration at the correct pH with buffer solution with valve **V** in load position **(a)**; the Tl solution was then loaded on CNTs at flow rate of 1.0 mL min^{-1}. When the sample has been loaded, the peristaltic pump **P** was stopped.

After the loading time, the conical micro-column, mounted at the furnace autosampler, was automatically moved into the dosing hole of the graphite tube and the retained metal was eluted with 75 µl of 1 mol L^{-1} nitric acid at a flow rate of 0.2 mL min^{-1} directly into the graphite furnace. After that, the autosampler arm was moved back to the origin position and the temperature program was started. During this period, the column was rinsed and conditioned. The absorbance measurements recorded as peak areas (s) were proportional to Tl concentration in the sample and were used for all measurements. The operating conditions were established and the determination was carried out.

Coupling of the packed micro-column with ETAAS

Owing to the discrete non-flow-through nature of the ETAAS, the limited capacity of the graphite tube and, the necessity for quantitative elution of the retained analyte, there are some difficulties when coupling the ETAAS directly with FI on-line sorption systems. In order to adapt the micro-column packed with CNTs to the requirements of ETAAS, the mass of the sorbent material was reduced as much as possible. The volume of CNTs busy in the new micro-column was 10 µL, while it was proved that 75 µL of 1.0 mol L^{-1} nitric acid was enough for quantitative elution.

Results and discussion

On-line pre-concentration conditions

Effect of pH

In order to optimize the adsorption conditions for the retention of thallium on CNTs, its signal was monitored by ETAAS while the pH of the solution that passes through the conical minicolumn was changed. pH is one of the most relevant variables to study since the overall process is typically dependent on the acidity conditions. It was experimentally verified that at pH values between 4.5 and 5.5 the retention is quantitative. Considering these results, the selected pH was 5.0.

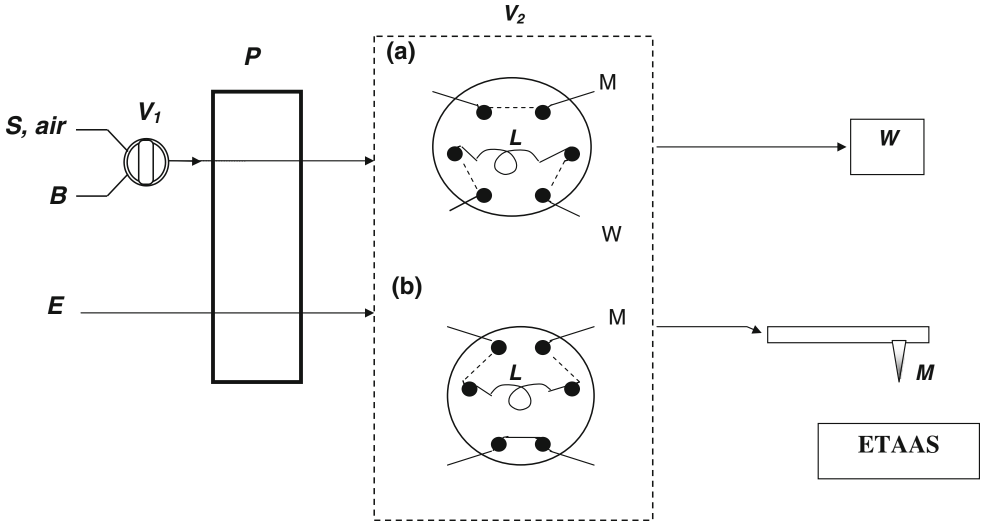

Fig. 1 Schematic diagram of the instrumental setup. $\mathbf{V_1}$ two way rotary valve; $\mathbf{V_2}$, six port rotary valve [(a) load position and (b) injection position]; **P**, peristaltic pump; **L**, sample loop; **S**, sample; **E**, eluent; **W**, waste; **M**, CNTs conical minicolumn

Effect of sample flow rate

The sample flow rate through the column packed with CNTs is a very important parameter, since this is one of steps that controls the time of analysis. We could verify that with flow rates up to 1.0 mL min^{-1} there was no effect on the analyte recovery.

Effect of eluent volume and concentration

Choice of a suitable eluent is very important for the successful coupling of an FI on-line sorption preconcentration manifold to ETAAS. A satisfactory eluent should effectively elute the adsorbed metal in a discrete volume, which is defined by the graphite tube capacity. The introduction of a strictly defined volume of eluent into the graphite tube was achieved using a simple volume based manifold (injection valve), as shown in Fig. 1. Airflow was employed to completely evacuate the packed column alter the loading step and also to deliver the eluent during the next step. For quantitative elution of the retained analyte in a small eluent volume, a low elution flow rate should be used, providing sufficient time for equilibrium between the solid phase and the eluent. The influence of the elution flow rate was studied in the range of 0.2–1.0 mL min^{-1}, and no significant variation in the thallium signal was observed. However, 0.2 mL min^{-1} flow rate was chosen as optimal. This fact was why the deposition of the eluent volume in the graphite tube and the reproducibility of the measurements were improved under such conditions.

Finally, in order to evaluate the elution of thallium adsorbed as a function of the eluent concentration, nitric acid solutions between 0.01 and 3.0 mol L^{-1} flowing at 0.2 mL min^{-1} were tested as eluent. The thallium signal was monitored in such range, and the best responses were obtained with 1.0 mol L^{-1} nitric acid solution. At lower concentrations, the elution was incomplete, and at higher concentrations, the background increased, with a consequent losses in precision and sensibility.

Graphite furnace temperature programs

The study of the best conditions for the graphite furnace temperature program was carried out by optimizing the pyrolysis and atomization steps. Since early experiences, showed that nitric acid was an effective eluent, and considering that hydrochloric acid could not be employed due to chloride interference [12], we optimize the temperature program in nitric acid media. Thus, in order to achieve the most suitable temperatures and hold times, the usual way of working with an AAS graphite furnace was followed.

Pyrolysis and atomization temperatures

The ramp time for the pyrolysis stage was carefully adjusted to allow gradual elimination of the matrix, avoiding any analyte loss by a sudden increase in temperature.

Figure 2 shows that a significant increase in the Tl signal was achieved in HNO_3 media when compared with an aqueous media. When Tl was in a HNO_3 media the maximum temperature without analyte losses achievable was around 700 °C, which is much more high than the common pyrolysis temperature used in aqueous media. This ensured complete matrix elimination.

The atomization temperature was varied within the range of 1,100 to 2,500 °C and the optimum temperature was observed at 2,100 °C. In addition, a hold time of 4 s was

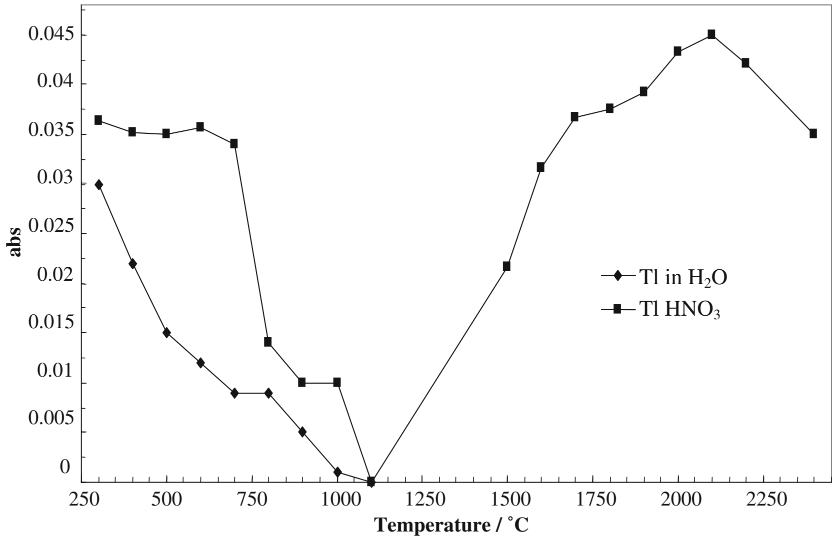

Fig. 2 Pyrolysis and atomization curve. Optimum conditions: pyrolysis at 700 °C and atomization at 2,100 °C in 1.0 mol L^{-1} nitric acid

Table 1 Procedures for pre-concentration and determination of thallium by ETAAS

Sample	Sample consumption	Limit of detection	Speciation	Enrichment factor	Reference
River sediment	0.1 g	0.015 µg L^{-1}	NO	27[a]	[17]
Wine	50 mL	0.05 µg L^{-1}	YES	50	[18]
Fresh water	1,000 mL	0.031 µg L^{-1}	YES	40	[21]
water	5 mL	0.05 µg L^{-1}	NO	10	[34]
water	2 mL	0.009 µg L^{-1}	YES	20	This work

[a] Enhancement factor

chosen for this step. No peak tailing or differences between standards and samples were observed under these conditions. A temperature of 2,200 °C and a hold time of 2 s were selected for the cleaning step.

Interferences

The thallium signal was preceded by excessive non-specific absorption when pyrolysis temperatures ≤600 °C were used. With a pyrolysis temperature of 700 °C the non-specific absorption at the beginning of the atomization stage could be eliminated, and using an atomization temperature of 2,100 °C, and no modifier, the atomic absorption could be separated from the background, making possible an interference-free determination of thallium.

The effects of representative potential interference species (at the concentration levels at which they may occur in the sample under study) were tested. Cd^{2+}, Co^{2+}, Cu^{2+}, Mg^{2+}, Mn^{2+}, Ni^{2+}, Pb^{2+}, and Zn^{2+} could be tolerated up to at least 5,000 µg L^{-1}. Commonly encountered matrix components such alkali and alkaline elements, and Cl^{-}, NO_3^{-}, and CO_3^{2-} are not retained on CNTs under the working conditions.

Analytical performance

Under the optimum conditions described above, the performance data of the on-line pre-concentration system for Tl determination were established. Table 1 shows a comparison between this method and others recently published for Tl determination by ETAAS.

The overall time required for the analysis of 2 mL of sample (2 min, at flow rate of 1 mL min^{-1}), elution (0.25 min, at flow rate of 0.2 mL min^{-1}), and data acquiring and conditioning (1 min) was about 3.25 min; hence, throughput sample was approximately 18 samples h^{-1}. The enrichment factor (EF) was calculated as the ratio between the slopes of the calibration curves obtained applying the pre-concentration procedure and directly by ETAAS, and was equal to 20.

The repetitivity of the pre-concentration method was evaluated by passing 2 mL of standard solution of Tl (I) (0.5 µg L^{-1}) through the minicolumn and repeating this procedure 10 times. The relative standard deviation (R.S.D.) was 4.0%, calculated from the peaks areas obtained. The reproducibility for real samples was also evaluated and was better than 4.0% in all cases. The calibration graph

Table 2 Recovery study applied to a real sample (95% confidence level, *n*=6)

Aliquots	Base value (µgL^{-1})	Quantity of Tl added (µgL^{-1})	Quantity of Tl found (µgL^{-1})	Recovery (%)[a]
1[b]	–	0.00	0.50±0.05	–
2[b]	0.50	0.50	0.98±0.03	96
3[b]	0.50	1.00	1.50±0.03	100
4[b]	0.50	2.00	2.47±0.04	98
5[b]	0.50	3.00	3.50±0.05	100
6[c]	–	0.00	N.D.	–
7[c]	0.00	0.50	0.50±0.05	100
8[c]	0.00	1.00	0.97±0.03	97
9[c]	0.00	2.00	1.95±0.05	97
10[c]	0.00	3.00	2.99±0.06	99

[a] 100 [(found base) / added]

[b] Study for Tl(I)

[c] Determination of Tl(III) as the difference between Tl(Total) and Tl(I)

using the pre-concentration system for Tl was linear with a correlation coefficient of 0.9992.

The limit of detection (LOD) was calculated as the amount of Tl required to yield a net peak equal to three times the standard deviation of the background signal (3σ criteria). The value of LOD obtained for the pre-concentration of 2 mL of aqueous solutions was 9 ng L^{-1}.

Validation study

In this case, the recovery study can be considered as a validation method [35] and we employed it in order to evaluate the accuracy of this method. Thus, twelve portions of drinking water of 2 mL each were analyzed. This method was applied to six portions (three for Tl(I) and three for Tl (III)) and the average quantity of each specie was taken as base value. Then increasing quantities of Tl(I) and Tl(III) were added to the other aliquots of sample. Table 2 shows a recovery test carried out in a real sample. The results were compared with the t-test and no significant differences were observed at 95% confidence level.

Finally, this procedure was applied to the determination of inorganic thallium species in drinking water samples. The data obtained indicated that the concentration of Tl(I) ranged from 0.5 to 2.0 μg L^{-1}. On the other hand, Tl(III) was not detected in all samples.

Conclusions

On the basis of the outcome of this study, carbon nanotubes (CNTs) have shown to be a suitable substrate for the pre-concentration of Tl(I). Furthermore, the matrix separation had the advantage of separating potential interferences for thallium determination by ETAAS. The on-line coupling of a solid phase extraction in a CNT minicolumn with ETAAS increased the speed of pre-concentration, reducing sample consumption and contamination risks, and improved the sensitivity and selectivity. The pre-concentration system was able to determine not only ultra-trace amounts of Tl, but also the amount of Tl(I) at ng L^{-1}levels in drinking water samples. Further research is needed in order to elucidate possible mechanism of sorption of various analytes of interest in this kind of materials. This understanding may expand the application field of CNTs in analytical chemistry, beyond the pre-concentration methods.

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