



King Saud University
Arabian Journal of Chemistry

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ORIGINAL ARTICLE

Speciation of Tl(III) and Tl(I) in hair samples by dispersive liquid–liquid microextraction based on solidification of floating organic droplet prior to flame atomic absorption spectrometry determination



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Received 14 October 2011; accepted 17 March 2012

Available online 25 March 2012

KEYWORDS

Dispersive liquid–liquid microextraction;
Thallium determination;
Hair samples;
Speciation;
Solidification

Abstract Dispersive liquid–liquid microextraction based on solidification of floating organic droplet was successfully used as a sample preparation method prior to flame atomic absorption determination of trace amounts of Tl(III) and Tl(I) in hair samples. In the proposed method, 1-(2-pyridylazo)-2-naphthol, 1-dodecanol and ethanol were used as chelating agent, extraction and dispersive solvent, respectively. Several factors that may be affected in the extraction process, such as type and volume of extraction and disperser solvents, pH, salting out effect, ionic strength and extraction time were studied. Under the optimal conditions, linearity was maintained between 6.0 and 900.0 ng mL⁻¹ for Tl(III). The relative standard deviation for seven replicate determinations of 0.2 μg mL⁻¹ Tl(III) was 2.5%. The detection limit based on 3S_b for Tl(III) in the original solution was 2.1 ng mL⁻¹. The proposed method has been applied for the determination of trace amounts of thallium in hair samples and satisfactory results were obtained.

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1. Introduction

Thallium (Tl) is a non-essential toxic element with no known beneficial biological role, which has various industrial applications (Riely and Siddiqui, 1986; Gao et al., 1985; Elson and Albuquerque, 1982; Baxter et al., 1997) such as semiconductors, nuclear medicine, catalysts, dyes and pigments. Tl is more toxic than mercury, lead, copper and cadmium (Rezaei et al., 2007) which can increase the risk of occupational poisoning

<http://dx.doi.org/10.1016/j.arabjc.2012.03.008>

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and environmental pollution. It exists usually in nature as Tl(I) and Tl(III) ion forms that exhibit different bioavailability and toxicity properties (Lan and Lin, 2005). Its monovalent state has higher stability, whereas its trivalent state forms complexes of greater stability.

Various methods have been reported for the determination of Tl including inductively coupled plasma-mass spectrometry (ICP-MS) (Das et al., 2006; Wei and Jiang, 1999), laser excited atomic fluorescence spectrometry (LEAFS) (Twining et al., 2003), X-ray fluorescence (Mihajlovic and Stafilov, 1998), electroanalytical methods (Dong et al., 2006; Spano et al., 2005) and electrothermal atomic absorption spectrometry (ETAAS) (Nukatsuka et al., 2004a; Saleh et al., 2001; Zendelovska and Stafilov, 2001). However, ICP-MS is an expensive analytical method and incurs high running cost, LEAFS is a less frequently used technique and direct analysis with ETAAS involves many difficulties because of spectral and non spectral interferences (Nukatsuka et al., 2004b).

Flame atomic absorption spectrometry (FAAS) combines a fast analysis time, a relative simplicity and a cheap cost. However, its main problem is low sensitivity for trace determination at $\mu\text{g L}^{-1}$ level. This limitation can be overcome by using separation and preconcentration procedures. For this purpose, several methods have been reported such as liquid–liquid extraction (Anthemidis et al., 2001; Zarei, 2007), co-precipitation (Soylak et al., 2005), flotation (Mohammad et al., 1994), hydride generation (Zhu and Xu, 2000) and solid phase extraction (Dadfarnia et al., 2007; Liang and Sang, 2008; Mashhadizadeh et al., 2004). However, these methods are labor, time and reagent consuming, and require a large volume of sample.

Separation and preconcentration procedures using liquid–liquid extraction generally result in a high-enrichment factor, owing to the difference between the volumes of the aqueous and organic phases. Although this procedure is operated in a batch mode, it is time consuming and produces large amounts of potentially toxic organic solvents as waste. These drawbacks could be overcome by the implementation of supplementary techniques in microextraction (Korna et al., 2006).

Recently, a liquid–liquid microextraction method namely, dispersive liquid–liquid microextraction (DLLME) was proposed (Rezaei et al., 2006). Furthermore, a new dispersive liquid–liquid microextraction method was also developed based on solidification of floating organic droplet (DLLME-SFO) (Xu et al., 2009). In this method, the enormous contact area between the organic droplets and sample solution is beneficial for the fast mass transfer from the aqueous phase to the organic phase. Accordingly, analysis time is shortened greatly and transfer of the solidified phase from aqueous phase can be carried out easily.

The aim of this work is the combination of DLLME-SFO and FAAS for developing a new method for the separation and preconcentration of trace amounts of Tl in hair samples. Speciation and effect of main factors were also investigated.

2. Experimental

2.1. Instrumentation

A SensAA GBC atomic absorption spectrometer (Dandenong, Australia) equipped with deuterium background correction

and air–acetylene burner was used for absorbance measurements according to the instrument instruction. Tl hollow cathode lamp was used as light source at wavelength of 276.8 nm. The operating parameters of the element were set according to the manufacturer's recommendation. The acetylene flow rate and burner height were adjusted in order to obtain the maximum absorbance signal, while aspirating the analyte solution. A Metrohm 692 pH meter (Herisau, Switzerland) was used for pH measurements. A Centurion scientific centrifuge model K241R (West Sussex, UK) was used to accelerate the phase separation.

2.2. Reagents and solutions

Deionized water was used throughout the experimental work. Stock solutions of Tl(I) and Tl(III) at a concentration of $1000.0 \mu\text{g mL}^{-1}$ were prepared by dissolving appropriate amounts of TlNO_3 and $\text{Tl}(\text{NO}_3)_3 \cdot 3\text{H}_2\text{O}$ (Merck, Darmstadt, Germany) in 0.5 mol L^{-1} HNO_3 solution. Working standard solutions were obtained by appropriate dilution of the stock standard solution. A solution of 1.2 mg mL^{-1} 1-(2-pyridylazo)-2-naphthol (PAN) (Merck) in ethanol was prepared. The solutions of alkali metal salt ($1\% \text{ w v}^{-1}$) and various metal salts ($0.1\% \text{ w v}^{-1}$) were used to study the interference of anions and cations, respectively. The laboratory glassware was kept overnight in a 1.4 mol L^{-1} HNO_3 solution and before using; all of the glasswares were washed with deionized water and dried.

2.3. DLLME-SFO procedure

All standards and samples were prepared for analysis according to the following procedure. Fifty milliliters of an aqueous solution containing $10.0 \mu\text{g}$ Tl(III) were placed in a test tube. To each test tube, 3.0 mL of 0.1 mol L^{-1} phosphate buffer (pH 10.0), 0.2 mL of 1.5 mg mL^{-1} PAN and 3.0 mL of $10\% \text{ (w v}^{-1}\text{) NaCl}$ were added. Then, 2.5 mL of ethanol containing $100.0 \mu\text{L}$ of 1-dodecanol (DOD) was injected rapidly into the sample solution. As a result, oil-in-water emulsions of DOD in water were formed. After centrifuging at 3000 rpm for 6.0 min , the organic solvent droplet due to lower density was floated on the surface of aqueous solution. Then, the test tube was put into an ice bath for 5.0 min ; as a result, the floated solvent was solidified because of the low melting point (24°C). Then, the solidified solvent was transferred to a conical test tube. The solidified solvent was washed by iced deionized water, and water in the vial was drawn out by a syringe. The solidified organic solvent was melted quickly in room temperature and 1.0 mL of 0.5 mol L^{-1} HNO_3 in methanol was added to it prior to the determination of Tl by FAAS.

After the oxidation of Tl(I) to Tl(III) (Vogel, 2000, London), total Tl was determined as Tl(III) by the above described method and concentration of Tl(I) is calculated by the difference between total Tl and Tl(III) concentrations. For this purpose, 35.0 mL of an aqueous solution containing Tl(I) and Tl(III) was taken in a volumetric flask. Then, 5.0 mL of Ce(IV) 0.01 mol L^{-1} and 5.0 mL of Mn(II) 0.01 mol L^{-1} were added to it. The solution was heated at 70.0°C for 30 min and cooled to room temperature and the final volume was completed up to 50.0 mL with deionized water.

2.4. Sample preparation

The hair sample has been prepared by using the procedure given in the literature (Dadfarnia et al., 2007). At first, hair samples were rinsed with acetone, chloroform and deionized water, and then dried at 60.0 °C. Ten grams of each sample hair was weighted accurately into a beaker and 15.0 mL concentrated HNO₃ was added to it. The content of each beaker was heated on a hot plate (initially at 100 °C for 15 min and then at 150 °C for 15 min) after dissolution. Then the mixture was heated at 200 °C to dryness and a white residue was obtained. After this, 10.0 mL of 0.1 mol L⁻¹ HNO₃ was added to the beaker and heated at 100 °C for several minutes. After this, the solution was cooled to room temperature and the final volume was adjusted to 50.0 mL with deionized water and Tl(III) was determined. To parallel, 10.0 g of the hair sample was prepared (Dadfarnia et al., 2007), then 2.5 mL of Ce(IV) and Mn(II) 0.01 mol L⁻¹ were added to it. After this, 10.0 mL of 0.1 mol L⁻¹ HNO₃ was added to the beaker and heated at 100 °C for several minutes. The solution was heated for 30.0 min at 70 °C. Finally, the solution was cooled to room temperature and the volume was adjusted to 50.0 mL with deionized water. The total Tl was determined according to the proposed procedure.

One certified reference alloy was also analyzed. Approximately 0.5 g of BCR, no. 288 was weighed accurately into a teflon cup and dissolved in concentrated HNO₃ (~5.0 mL) with heating on a water bath. Then, 15.0 mL deionized water was added to it and oxidation of Tl(I) to Tl(III) has been performed by using the given procedure in Section 2.3. Finally, the solution was cooled and diluted to 100.0 mL with deionized water in a calibrated flask.

3. Results and Discussion

In order to obtain a suitable sensitivity in speciation and determination of Tl ions, combination of DLLME-SFO with FAAS was developed. The effect of different parameters such as type and volume of extraction and disperser solvents, pH, ionic strength, concentration of the chelating agent and salt addition on the extraction efficiency was investigated and optimized. Working solutions containing 10.0 µg Tl were used and the measurements were replicated for three times.

3.1. Selection of type and volume of disperser solvent

Mixing of the disperser solvent with extraction solvent and sample solution is significant for choosing the disperser solvent. For this purpose, acetone, ethanol and methanol were selected as candidates of disperser solvent. For the selection of appropriate disperser solvent, a series of sample solutions containing Tl(III)-PAN complex were extracted using 2.5 mL of each mentioned disperser solvent containing 100.0 µL of DOD. The recoveries for acetone, ethanol and methanol were 98.4%, 97.6% and 99.3%, respectively. The higher recovery was obtained using methanol but ethanol has low toxicity and cost, therefore, it was selected as disperser solvent.

To obtain the optimized volume of ethanol, various experiments were performed using different volumes of ethanol (1.0–5.0 mL) containing 100.0 µL of DOD. The results showed that the recovery increased up to 2.0 mL and decreased in the

higher volume of 3.5 mL. This trend can be probably contributed to that at low volume, ethanol could not disperse DOD properly and cloudy solution was not formed completely. Reversely, at high volumes, the solubility of the complex in water increased. Finally, 2.5 mL ethanol was chosen as the optimum volume.

3.2. Selection of type and volume of extraction solvent

The extraction solvent is important in the optimization of the DLLME-SFO process. For the selection of this solvent, its low solubility in water, high affinity to analytes, and lower melting point than room temperature and lower density than water are important. In this work, 1-undecanol and 1-dodecanol were investigated as extraction solvents, and their recovery were studied. The recoveries for 1-undecanol and DOD were 97.3% and 98.7%, respectively, and also 1-undecanol is more expensive than DOD. Thus DOD was selected as extraction solvent in the next experiments.

The effect of DOD volume on the recovery of Tl was also investigated over the range of 40.0–200.0 µL with 2.5 mL ethanol. The results showed that the recovery increased to 75.0 µL and remained constant. Based on these observations, 100.0 µL was selected for further experiments.

3.3. Influence of pH

The effect of pH on the recovery of Tl(III) ions was studied in the range of 3.0–12.0. The pH of sample solutions were adjusted by the addition of HNO₃ and NaOH solutions. The results are given in Fig. 1 and show that the highest recovery was obtained at a pH range of 9.5–12.0. Additional experiments on the volume of buffer showed that 2.0–8.0 mL of buffer solution (pH 10.0) gives the best results. Therefore, 3.0 mL of 0.1 mol L⁻¹ phosphate buffer solution was used in all subsequent experiments.

3.4. Effect of the PAN concentration

Tl(I) cannot form the complex with PAN. The influence of PAN concentration on the recovery of Tl(III) ions was studied in the concentration range of 0.1–2.5 mg mL⁻¹. For this purpose, var-

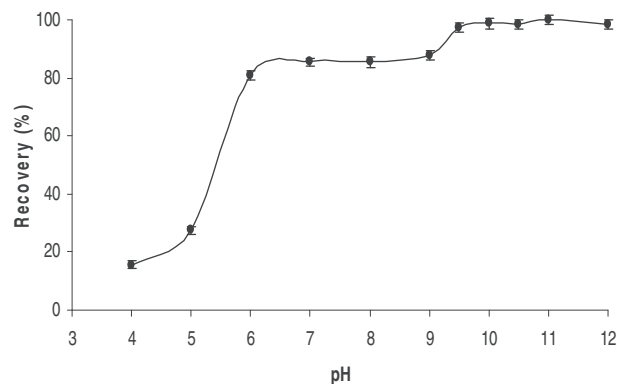


Figure 1 Effect of the solution pH on the DLLME-SFO extraction of Tl(III). Conditions: sample, 50.0 mL Tl(III) 0.2 µg mL⁻¹; buffer, 3.0 mL; PAN 1.2 mg mL⁻¹, 0.2 mL; NaCl 10% (w v⁻¹), 3.0 mL and DOD, 100.0 µL.

Table 1 Tolerance limit for various species in determination of 10 µg of Tl(III).

Foreign ions	Tolerance limit ($W_{\text{interference}}/W_{\text{Tl(III)}}$)
PO_4^{3-} , HPO_4^{2-}	3000
Ca^{2+} , Mg^{2+}	1500
Cr^{3+}	600
Pb^{2+} , Ag^+	500
Fe^{3+}	300
Co^{2+}	150
Ni^{2+}	100
Cd^{2+}	250
Cu^{2+} , Zn^{2+}	200
Humic acid	300
Al^{3+}	50

Conditions were the same as Fig 1.

ious experiments were performed using 0.2 mL of PAN. The results showed that the recovery increased to 0.5 mg mL⁻¹ and then remained constant. Therefore, a PAN concentration of 1.5 mg mL⁻¹ was selected in all further experiments to account for the other extractable species that potentially interfere with the assaying of Tl.

3.5. Effect of the ionic strength

In the extraction, the solubility of many analytes in aqueous solutions decreases with increasing ionic strength due to salting

out effect (Mohammadi et al., 2009a,b). The influence of the ionic strength on the extraction of Tl(III) was studied with sodium chloride solution in the range of 0.05–1.0 g. The rest of the experimental conditions were kept constant. The recovery increased up to 0.2 g and for higher amounts it was constant. Therefore, 0.3 g of NaCl was used in all further experiments.

3.6. Effect of extraction time

In order to have a good precision, sensitivity and speed, it is necessary to select an extraction time that guarantees the achievement of equilibrium between aqueous and organic phase. In DLLME, extraction time is defined as the time interval between injection of the mixture of disperser and extraction solvents and starting of centrifuge. The effect of extraction time on the recovery was studied by varying the extraction time from 0.5 to 15.0 min while the other experimental conditions were kept constant. The results showed that the extraction time had no influence on the recovery of Tl(III) ions. This can be contributed to the increase in surface area between extraction solvent and aqueous phase after the formation of a cloudy solution. This behavior has also been seen in DLLME (Mohammadi et al., 2009b; Ma et al., 2009; Rezaei et al., 2008).

3.7. Calibration, precision and detection limit

Linearity, repeatability and detection limit were investigated under the optimized experimental conditions. For a sample

Table 2 Determination of Tl in hair samples.

Sample	Tl amount (µg g ⁻¹)		Recovery (%)
	Added	Found ^a	
Hair sample no. 1	Tl ⁺ : 0.00	Tl ⁺ : 0.021 ± 0.001	–
	Tl ³⁺ : 0.00	Tl ³⁺ : 0.037 ± 0.002	–
	Tl ⁺ : 0.05	Tl ⁺ : 0.073 ± 0.004	104
	Tl ³⁺ : 0.05	Tl ³⁺ : 0.088 ± 0.005	102
Hair sample no. 2	Tl ⁺ : 0.00	Tl ⁺ : 0.027 ± 0.002	–
	Tl ³⁺ : 0.00	Tl ³⁺ : 0.034 ± 0.003	–
	Tl ⁺ : 0.05	Tl ⁺ : 0.075 ± 0.005	96
	Tl ³⁺ : 0.05	Tl ³⁺ : 0.085 ± 0.003	102

^a Mean ± standard deviation ($n = 3$).

Table 3 Comparison of the reported methods with the proposed method.

Enrichment method	Detection method	Speciation analysis	Enhancement factor	Detection limit (ng mL ⁻¹)	Reference
SPE ^a	FIA-FAAS ^b	Yes	77	2.5	Dadfarnia et al. (2007)
SDME ^c	ETAAS ^d	No	50	0.7	Chamsaz et al. (2009)
LLE ^c	FAAS	No	–	4	Rajesh and Subramanian (2006)
SPE	FAAS	No	–	1	Taher (2003)
DLLME	FAAS	Yes	42.7	2.1	This work

^a Solid phase extraction.

^b Flow injection analysis.

^c Single drop microextraction.

^d Electrothermal atomic absorption spectrometry.

^e Liquid–liquid extraction.

volume of 50.0 mL, the calibration curve exhibited a linearity over the range of 6.0–900.0 ng mL⁻¹ with a correlation coefficient of 0.9987 ($A = 0.685C + 0.002$, where A is the absorbance value and C is the concentration of Tl(III) (μg mL⁻¹)). Seven replicate determinations of 0.2 μg mL⁻¹ Tl(III) gave a mean absorbance of 0.134 with a relative standard deviation of 2.5%. Preconcentration of 50.0 mL of sample permitted the detection limit ($3S_b$) of 2.1 ng mL⁻¹ for Tl(III) ion.

The enhancement factor, defined as the ratio of the slope of the calibration curve for the DLLME-SFO procedure to that obtained without preconcentration (Ma et al., 2010), was 42.7.

3.8. Effect of diverse ions

In order to examine the effect of common coexisting ions on the extraction of Tl(III) different metal cations and anions were added individually to a sample solution containing 10.0 μg of analyte (Table 1). The tolerance limit was set as an amount of the interfering ion required to cause ±5% error. As can be seen in Table 1, most of the examined cations and anions did not interfere with the extraction and determination of Tl(III) even when present in 100-fold excess over Tl(III). This shows that the proposed method is suitable for the determination of Tl(III) in real samples.

3.9. Accuracy of the method

Accuracy of the proposed method has been evaluated for the determination of Tl(III) ion in BCR no. 288. The amount of Tl in BCR was found to be $2.26 \pm 0.11 \mu\text{g g}^{-1}$. It was found that there is no significant difference between the result obtained by the DLLME-SFO procedure and the certified result ($2.3 \pm 0.1 \mu\text{g g}^{-1}$).

3.10. Analysis of real samples

The DLLME-SFO procedure has been applied for the determination of Tl content in hair samples. Furthermore, to evaluate the validity of the DLLME-SFO procedure for speciation of Tl, recovery of different amounts of Tl(I) and Tl(III) ions added to hair samples were also studied. The results are given in Table 2. The results indicate that the added Tl(I) and Tl(III) ions can be quantitatively recovered from hair samples by the proposed procedure. These results demonstrate the applicability of the proposed procedure for Tl determination in hair samples.

4. Conclusions

This work has demonstrated that the combination of DLLME-SFO with flame atomic absorption spectrometry provides a novel route for speciation and determination of Tl ions in hair samples. The main benefits of the DLLME-SFO method are: minimum use of toxic organic solvent, simplicity, low cost and enhancement of sensitivity.

A comparison of the proposed method with the other reported methods (Taher, 2003; Rajesh and Subramanian, 2006; Dadfarnia et al., 2007; Chamsaz et al., 2009) is shown in Table 3. According to this table, the enrichment factor and the detection limit obtained by the proposed method are comparable to those in reported methods.

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