

Evaluation of thallium rate in soil after dispersive liquid-liquid micro-extraction

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Abstract

Thallium is widely found in nature, but the only inorganic stones full of this element are crookesite and lorandit. It is also found in pyrites of copper, lead and inorganic stones. The element and its compositions are toxic and harmful to the environment; therefore, its application requires caution and further research. It is important to develop sensitive and accurate analytical methods to determine trace levels of thallium in environmental and real samples. In this research, dispersive liquid-liquid microextraction based on solidification of floating organic drop as a sample preparation method was used for separation and preconcentration of ultra-trace amounts of thallium in soil samples prior to graphite-furnace atomic-absorption spectrometry. Investigated effective parameters on extraction include pH, the amount of chelating agent, type and volume of extraction solvent and extraction time. Under optimum conditions, the calibration curve was linear in the range of 0.2-10.0 ng mL⁻¹ of thallium in the original solution, with limit of detection of 0.03 ng mL⁻¹. The relative standard deviation (RSD) for ten replicated determinations of thallium ion at 5.0 ng mL⁻¹ concentration level was calculated as 3.3%. The proposed method was successfully applied to the determination of thallium in soil samples.

Keywords: Soil samples; thallium determination; dispersive liquid-liquid microextraction; graphite-furnace atomic-absorption spectrometry

1. Introduction

Any change in specifications of soil constituents that make soil impossible to use is called soil pollution (Asami *et al.*, 1996). Recently, safely removing waste from human environments has emerged as essential for the survival of civilization. In order to minimize pollution, waste needs to be quickly returned to its natural cycle. Soil is a medium of waste recovery. Soil's capability for surface absorption, exchange, oxidation and sedimentation of matters is important for both polluted matters and also nutrition of plants (Janssen and Hogervorst,

1993). Soil pollution by toxic elements usually results from human activities. Soil contamination from factories, urban and industrial wastes, insecticides, and traffic pollution can maximize the concentrations of toxic elements in soil (Breimer *et al.*, 1989). To see the most serious effects of the aggregation of toxic metals in soils we should look at animals whose pasture is limited to polluted districts. Study of effects on vegetables shows that some pesticides, such as organic chloride insecticides, not only may change the plant environment for the worse, but may also pollute different parts of the biosphere through transmission and absorption in fatty tissues, finally entering the food chain and endangering the lives of human and animals (Gworek, 1992). Thallium (Tl) is a weak, soft, grey and tin form metal that is discoloured in the

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vicinity of air (Hawley *et al.*, 1993). Tl and its compounds are very poisonous. This toxicity results from its ability to replace alkaline metals, including sodium and potassium, in the body. This will disrupt many cellular processes. The element is therefore used in the production of rat poison and insecticides, but such applications are prohibited in many countries. It is also used in infrared sensors. It can even have criminal uses as a poison, much like arsenic (it is also known as the "inheritance powder") (Arzate and Santamaria, 1998). Some symptoms of thallium poisoning are hair loss and damage to the areas around nerves (poisoned persons often report feeling like they are walking on hot coal). Thallium combinations are highly soluble in water; contact of more than 0.1 mg m⁻² with skin for eight hours is equal to 40 working hours a week. It is suspected of being a carcinogen in human beings. It was used often used as a murder poison when its antidote, Prussian blue, had not yet been discovered (Gao *et al.*, 1985). It is very difficult to measure thallium in environmental samples due to the low concentration of this element and also the effect of other disturbing elements (Jamshidi *et al.*, 2011). A large number of techniques have been employed for the determination of traces of Tl in environmental samples, such as electrochemical methods (Lee *et al.*, 2008), inductively coupled plasma-mass spectrometry (Escudero *et al.*, 2013), flame atomic-absorption spectrometry (FAAS) (Otruba *et al.*, 1984) and graphite-furnace atomic-absorption spectrometry (GFAAS) (Afzali *et al.*, 2013). Among these techniques, GFAAS has been most successfully employed in determination of Tl species due to its reliability, sensitivity, and relatively low cost. The determination of extremely low concentration of elements usually requires a separation and a preconcentration step. For this purpose, many different techniques have been used, including solid-phase extraction (Nukatsuka *et al.*, 2004), liquid-liquid extraction (Afzali *et al.*, 2013), single-drop micro-extraction (Chamsaz *et al.*, 2009), and separation and preconcentration use of micro-column (Dadfarnia *et al.*, 2009). However, in recent years liquid-phase microextraction (LPME) techniques have received a growing amount of attention due to their simplicity, low consumption of organic solvent, low cost, ease of operation, and potential for high enrichment factor (Dadfarnia and Haji Shabani, 2010). Combination of microextraction systems and ultrasound radiation provides an efficient

preconcentration technique for determination of analytes at trace levels (Regueiro *et al.*, 2008). In this research, we coupled dispersive liquid-liquid microextraction based on solidification of floating organic drop as a sample preparation method with ultrasound for separation and preconcentration of an ultra-trace amount of thallium prior to GFAAS. Mass transfer between matters placed in two different phases was also performed using supersonic waves and supersonic waves caused by ultrasound replaced dispersive solvent, which was omitted. The applicability of the approach was demonstrated for the determination of thallium in soil samples. Factors affecting the extraction efficiency, such as solution pH, type and volume of extraction solvent, the amount of chelating agent and extraction time, were optimized.

2. Material and methods

0.4 ng mL⁻¹ of thallium solution and 200 μ L of ligand of 1-(2-Pyridylazo)-2-naphthol (PAN) 0.05% was adjusted to pH 5.5 by acetate buffer and poured in a volume of 8 mL into a screw-cap glass conical flask. Then, 40.0 μ L of 1-undecanol was injected into the sample solution by a Hamilton syringe and sonicated for six minutes. A cloudy solution was formed in the flask and the Tl-PAN complex was extracted into the fine droplets of 1-undecanol. This turbid solution was then centrifuged at 4000 rpm for five minutes and the extraction solvent floated on the surface of aqueous solution. The glass flask was transferred to an ice bath. Organic solvent was solidified over five minutes and transferred into a conical vial, where it immediately melted. The volume of solid phase was 40 \pm 1 μ L. 20.0 μ L of this phase was injected into the GFAAS for analysis.

3. Results and discussion

In this research, the effects of different parameters affecting complex formation and extraction conditions such as pH, amount of ligand, type and volume of extracting solvent, extraction time and interfering ions were investigated. Then, the amount of thallium in soil samples was evaluated using a dispersive liquid-liquid microextraction method.

3.1. Effect of pH

Dispersive liquid-liquid microextraction based on solidification of floating organic drop requires

formation of a complex with suitable hydrophobicity for separation of metal ions. This complex needs to extract organic solvent with a small volume of floating phase. pH plays a critical role in the formation of metal cations' complex and stability. The effect of sample pH on the extraction of thallium was studied by varying the pH within the range of 1.0–10.0 using sodium acetate, potassium phosphate, ammoniac, nitric acid, acetic acid, phosphoric acid and sodium hydroxide. Figure 1 shows the results. It can be seen that the recoveries are nearly constant in the range 5.0–7.5; therefore, pH=5.5 was chosen for subsequent experiments. At lower pHs, it is possible to compete H^+ and protonate ligand; at higher pHs, $Tl(OH)_3$ may be sediment, and the recovery percentage reduces.

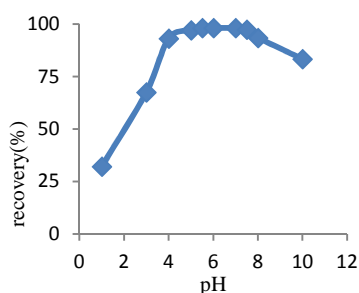


Fig. 1. Effect of pH on recovery percentage of thallium

3.2. Effect of Ligand

The effect of 0.05% (w/v) 1-(2-Pyridylazo)-2-naphthol on the extraction recovery of thallium was evaluated in the range of 20–500 μ L. The results show that recovery percentage increases with an increase of the volume of ligand up to 300 μ L; above this volume, recovery will be reduced a little. The ligand is extracted into the extraction phase and saturates it (Fig. 2). Therefore, a volume of 200 μ L was selected as the optimized volume.

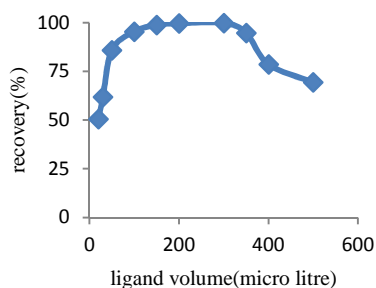


Fig. 2. Effect of volume of 1-(2-Pyridylazo)-2-naphthol 0.05% on recovery percentage of thallium

3.3. Effect of Type and Volume of Extracting Solvent

Special attention shall be paid to the selection of the type of extracting solvent. It must have a lower density than water, high extraction capability for the compounds of interest, low volatility, low water solubility and a melting point near room temperature. In this case, 1-undecanol, 1- dodecanol and normal hexadecane were studied. 1-undecanol was selected because of higher extraction efficiency, sensitivity, stability, lower price, low water solubility and low vapour pressure.

In order to examine the effect of the extraction solvent volume, different volumes of 1-undecanol (10.0–45.0 μ L) were used as the extraction solvent for the mentioned procedure. The presented results show that as the volume of 1-undecanol increases, the volume of floating phase rises; therefore, the enrichment factor reduces (Fig. 3). Hence, the highest enrichment factor is achieved at volume 40.0 μ L of 1-undecanol. Since 40 ± 1 μ L of floating phase was obtained by using a volume of 40.0 μ L, the volume of 20.0 μ L was injected to graphite furnace. Therefore, 40 μ L of 1-undecanol was chosen as the optimized volume for the next tests.

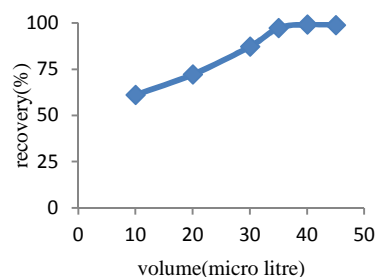


Fig. 3. Effect of volume of 1-undecanol on recovery percentage of thallium

3.4. Effect of Extraction Time

Extraction time is an important factor in almost all extraction methods. In this method, the extraction time is considered as the time interval from the injection of extracting solvent to the end of the supersonic waves bath. The effect of extraction time was thus evaluated in the range of 3–14 min. The results showed that the extraction increased for seven minutes then remained fixed. It seems that separation is not well performed in shorter times (Fig. 4). As already shown, thallium recovery percentage is relatively independent of

extraction time, because the kinetics of the contact level are greater than in the extraction phase with water solution. According to these observations, the extraction time for the next tests was considered to be 10 minutes.

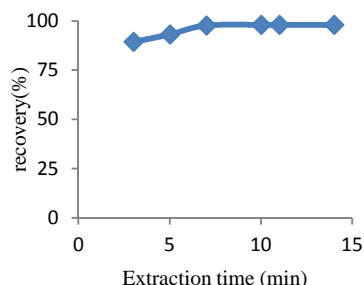


Fig. 4. Effect of extraction time on recovery percentage of thallium

Table 1. Study of Different Bothering Ions in Extraction & Pre-Concentration of Thallium

Ion	Bothering Limit (Concentration Proportion of Bothering Ion to Thallium)
Ca ²⁺ , Mg ²⁺	1500
Mn ²⁺	260
Zn ²⁺	130
Pb ²⁺ , Sn ²⁺ , Cd ²⁺ , Co ²⁺	70
Ni ²⁺ , Hg ²⁺ , Ag ⁺	55
Al ³⁺	40

4.4. Figures of merit

The analytical figure of merit was evaluated for the determination of thallium according to the recommended procedure under optimized

3.4. Effect of Interfering Ions

The effect of interfering ions on extraction of thallium was studied. For this purpose, a number of solutions with volume 8 mL and concentration of thallium 0.4 ng mL⁻¹ with pH = 5.5 and various amounts of other ions, were prepared and extracted according to the described procedure. Concentration of extracted thallium was measured with GFAAS. The amount of ion causing a variation of more than ±5% in absorbance of thallium was considered a potentially interfering ion. The obtained results are shown in Table 1.

conditions. Table 2 indicates some of the analytical factors of the method, including enrichment factor, limit of detection, relative standard deviation, correlation coefficient, and linear range.

Table 2. Some Analytical Parameters in Thallium Measurement

Parameter	Analytical Rate
Linear Scope (Ng/ml)	0.1-6.0
Grading Curve Equation (Ng/ml)	Y= 0.0304x+0.006
Grading Curve Correlation Coefficient (R ²)	0.9966
Recognition Limit (Ng/ml)	0.03
Relative Standard Deviation (%) (n=10) (Con: 5.0 Ng/ml)	3.34%
Sample Volume (ml)	8
Concentration Factor	200.0
Extraction Time (minutes)	10

4.5. Thallium Measurement in Real Samples

In order to study the ability of the method to be used in real samples with different tissues, it was employed for separation, preconcentration and measurement of thallium in the soil samples.

In order to analyse the method's validity, defined amounts of thallium were added to each soil sample, and thallium extraction and recovery of the solutions were performed (Table 3).

Table 3. Thallium Measurement in Soil Samples

Sample on Test	Found Rate (Ng/ml)
Zarand Agricultural Soil	2.08±0.04
Baft Agricultural Soil	1.02±0.09
Jiroft Agricultural Soil	2.62±0.13
Rafsanjan Agricultural Soil	1.28±0.06

Average of three tests± standard deviation

4. Conclusion

Since the thallium concentration in nature is very low, and its measurement in real samples is very important due to its toxicity and harmfulness to the environment, analytical chemistry needs methods with high sensitivity and selectivity for determining and measuring this element in the environment and in real samples. In this study, dispersive liquid-liquid microextraction based on solidification of floating organic drop prior to graphite-furnace atomic-absorption spectrometry determination, has been developed for separation and sensitive determination of thallium in aqueous samples. The application of ultrasonic radiation is a powerful aid for improving the extraction efficiency of the extraction procedure in the lowest possible time. The main advantages of this method are minimum use of organic solvents, non-use of toxic organic solvents, simplicity, high sensitivity and rapid analysis time.

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