

Preconcentration and determination of thallium in human plasma by flame atomic absorption spectrometry after ion pair solvent microextraction

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ABSTRACT

A simple, rapid and cost effective preconcentration method is described for the determination of thallium in aqueous samples and human plasma using ion pair solvent microextraction (IP-SME) followed by flame atomic absorption spectrometry (FAAS). In trace element analysis, preconcentration and separation methods enhance the sensitivity and precision of the determination. In a preconcentration step 10 ml of Tl solution was adjusted at pH=8 and treated with 2ml of 0.1 % 2-pyridyn mercaptan (PyM) transferred to a 15ml vial. Thallium formed a cationic complex with 2-pyridyn mercaptan. For creating ion pair and converted cationic complex to nonpolar form, 0.5 ml of 1% picric acid, as a counter ion, was added to the sample solution. The solution was stirred by a magnetic stirrer with a 6-mm bar at an optimized speed of 500 rpm. The ion-pair, $(Tl-PyM)^+$ (picrate) $^-$ was formed and extracted by the acceptor phase consisting 4 μ l of nitrobenzene for 10 min. After extraction, the microdrop was retracted and to be measured by FAAS the drop volume was brought to 50 μ l by acetone. Resulting solution directly injected into the nebulizer of AAS by a micro syringe for subsequent determination. Some effective parameters on extraction and complex formation, such as type and volume of organic solvent, pH, concentration of chelating agent and counter ion, extraction time and stirring rate were optimized. Under the optimum conditions, the enrichment factor and recovery were 188.0 and 94.0%, respectively. The calibration graph was linear in the range of 12 - 130 μ g L $^{-1}$ with correlation coefficient of 0.9989 under the optimum conditions of the recommended procedure. The detection limit based on the $3S_b$ criterion was 3.6 μ g L $^{-1}$ and relative standard deviation for (RSD) for ten replicate measurements of 50 μ g L $^{-1}$ and 100 μ g L $^{-1}$ lead was 4.9 and 4.7 % respectively. The results for determination of thallium in reference materials and human plasma demonstrated the accuracy, recovery and applicability of the presented method.

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KEYWORDS

Ion pair solvent
microextraction;
Preconcentration;
Atomic absorption spectrometry;
Thallium.

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INTRODUCTION

Heavy metals have long been known as a major contamination problem, not only for working conditions but also for the environment^[1,2]. Heavy metals contamination may occur due to irrigation with contaminated water, the addition of fertilizers, metal based pesticides, industrial emissions, transportation, harvesting process and storage. Heavy metals are general terms, which apply to the group of metals and metalloids with atomic density greater than 4 g cm^{-3} ^[3-6]. Metals and other elements can be naturally present in food or can enter food as a result of human activities such as industrial and agricultural processes. The metals of particular concern in relation to harmful effects on health are heavy metals such as thallium, mercury, cadmium and lead. Heavy metals are among the major contaminant of food supply and are considered as problem to the environment^[7].

Thallium is a non-essential toxic element with no known beneficial biological role, which has various industrial applications^[8-11] such as semiconductors, nuclear medicine, catalysts, dyes and pigments; thereby increasing the risk of occupational poisoning and environmental pollution. 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^[12]. It is known that Tl (I) is highly toxic to the biosphere even more toxic than Hg, Pb, Cu and Cd^[13,14]. Fortunately, Tl concentration in environmental samples is generally quite low. Its concentration in surface water usually is in the range of 10–100 ng L⁻¹^[15] whereas in non-polluted soils lies typically between 0.3 and 0.55 mg kg⁻¹^[16]. Thus development of new methods for selective determination of Tl in sub micro levels especially in human plasma is of continuing interest which needs separation and preconcentration steps prior to analysis. The most widely used techniques for separation and preconcentration of trace thallium include liquid-liquid extraction^[17,18] and solid phase extraction^[19-22] have been used for analyte sample enrichment. Various solid materials such as ion exchange^[23], ac-

tivated carbon^[24] and microcrystalline naphthalene^[25] have been used for preconcentration of trace metals.

Using toxic organic solvent in extraction methods is a great problem. Solvent microextraction technique effectively overcomes these difficulties by reducing the amount of organic solvent and by allowing sample extraction and preconcentration to be done in a single step. The technique is faster and simpler than conventional methods. It is also inexpensive, sensitive and effective for the removal of interfering matrices. Solvent microextraction is a form of solvent extraction with phase ratio values higher than 100^[35-39]. This technique uses simple equipment which is found in most analytical laboratories and also has been used for sample preparation of organic components and has coupled with chromatography methods. We developed this technique in our laboratory and reported for the first time on the coupling of solvent microextraction (SME) with spectrometry to determine inorganic compounds^[35].

Different analytical techniques have been performed to determine thallium in various samples including flame atomic absorption spectrometry (FAAS)^[26,27], graphite furnace atomic absorption spectrometry (GFAAS)^[28], inductively coupled plasma emission spectrometry (ICP-OES)^[29], inductively coupled plasma mass spectrometry (ICP-MS)^[30-33].

The aim of this work is to combine solvent microextraction with FAAS and develop a new method for the determination of trace Tl in aqueous solutions and human plasma. Ion pair complex of 2-pyridyl mercaptan and picrate with thallium was extracted from aqueous solution into the microdrop and then determined by flame atomic absorption spectrometry. The factors influencing the efficiency of solvent microextraction and FAAS determination were systematically studied. The method was successfully applied to determine trace amounts of Tl in standard samples and human plasma.

EXPERIMENTAL

Reagent and materials

All reagents were of analytical grades. A stock

solution of 1000 $\mu\text{g L}^{-1}$ Tl(I) was prepared by dissolving the appropriate amounts of thallium nitrate (Merck, Darmstadt Germany) in 1% HNO_3 . More diluting solutions were prepared daily from the stock solution. The extraction organic phase was nitrobenzene (Merck, Darmstadt, Germany). A 2.0% (w/v) 2-pyridyn mercaptan (PyM) (Aldrich, USA) solution was prepared by dissolving 2 g of PyM in 100 ml acetone which was used as a complexing agent. A 1% (m/v) picric acid (Wako Pure Chemicals) solution was prepared acting as the counter ion. All other chemicals used in this work were of analytical-reagent grade; double-distilled water was used throughout.

Instrumentation

The experiments were performed using a Shimadzu atomic absorption spectrometer (AA 6300), was used for determination of thallium using an air-acetylene flame. Thallium hollow cathode lamp (Hamamatsu photonics, Kyoto, Japan) was used as a radiation source adjusted at the operating current to the value recommended by the manufacturer. The operating conditions were as follows: wavelength 276.8 nm, lamp current 5.0 mA and spectral bandwidth of 0.5 nm. The acetylene flow and the air flow were 1.8 and 8 Lmin^{-1} , respectively. The pH values were determined with a Metrohm digital pH meter (model: 781, Herisua, Switzerland) with a combined glass electrode. A 50 μl Hamilton 7105 syringe (Hamilton, Reno, NY, USA) was used to suspend the drop of the acceptor phase and to inject finally solution into the atomic absorption spectrometer. Samples were stirred in 15 ml flat-bottom vials containing Teflon-line septa using an electronic magnetic stirrer (VWR Scientific, West Chaster, PA, USA).

Analytical procedure

10 ml of Tl solution was adjusted at $\text{pH}=8$ and treated with 2ml of 0.1 % 2-pyridyn mercaptan transferred to a 15ml vial. Thallium formed a cationic complex with 2-pyridyn mercaptan. For creating ion pair and converted cationic complex to nonpolar form, 0.5 ml of 1% picric acid as a counter ion, was added to the sample solution. The solution was stirred by a magnetic stirrer with a 6-mm bar at an optimized speed of 500 rpm. The ion pair, $(\text{Tl}-\text{PyM})^+$

(picrate)⁻, was formed and extracted by the acceptor phase consisting 4 μl of nitrobenzene for 12 min. The 4 μl acceptor phase was suspended at the tip of a Hamilton syringe, clamped in such a way that its tip was located at a fixed position inside the aqueous solution. After the extraction, the microdrop was retracted and to be measured by FAAS the drop volume was brought to 50 μl by acetone. Resulting solution directly injected into the nebulizer of AAS by a micro syringe for subsequent determination. For injection of solution directly into the nebulizer the plastic capillary tube attached to the nebulizer was removed and needle of syringe was inserted directly into the nebulizer. The parameters affecting the complexation and extraction efficiency were optimized.

RESULTS AND DISCUSSION

It is essential to optimize all the parameters affecting the performance of solvent microextraction of thallium from the aqueous samples is essential. These include type and volume of organic solvent, pH, concentration of chelating agent and counter ion, extraction time and stirring rate. The effects of each parameter on the extraction process were examined and the results are as follows. After optimization this method was used for extraction, preconcentration and determination of trace amounts cadmium in aqueous solutions and human plasma.

Solvent type

The type of extraction solvent used in SME is an essential consideration for efficient extraction. Five solvents, i.e., chloroform, carbon tetrachloride, dichloromethane, benzyl alcohol and nitrobenzene were tested for the extraction of thallium from 10 ml of 50 $\mu\text{g L}^{-1}$ solution. As can be seen in Figure 1, nitro benzene was found to provide higher extraction efficiency of thallium ion pair complex.

pH

The effect of pH on the complex and ion pair formation and extraction of thallium from aqueous samples was studied within the range of 3.0 -12.0. Figure 2 shows the influence of pH on the extraction of cadmium. As can be seen in Figure 2, the extraction system provided the highest efficiency at pH of around 8. The pH of the primary solution of cad-

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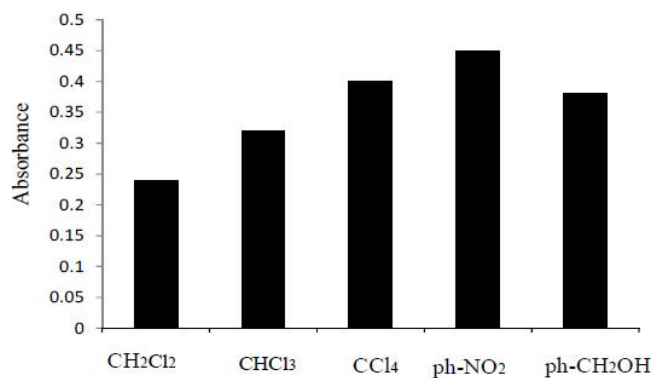


Figure 1 : Effect of type of extraction solvent on the absorbance obtained from SME

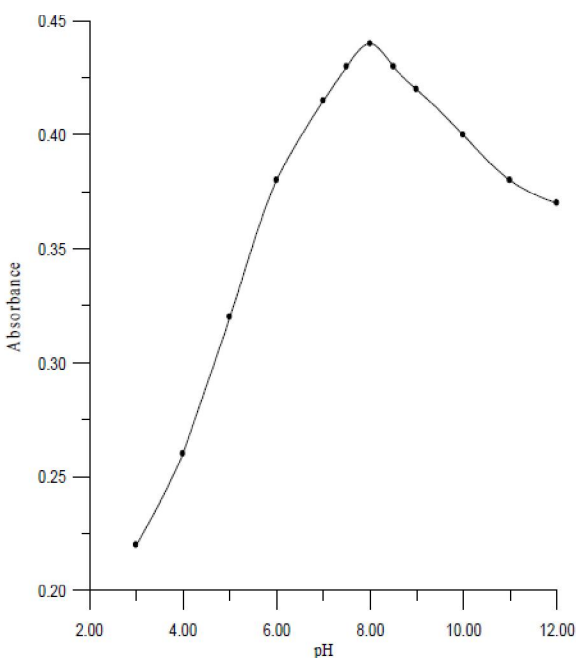


Figure 2 : Effect of pH on the absorbance of cadmium obtained from SME

mium with picric acid was 3. The Absorbance was increased at a pH value around 8 because the dissociation of picric acid to picrat increases the formation of ion pair and hence its transfer into the single drop. At higher pH values there was a decrease in the absorbance probably due to the precipitation of thallium hydroxide hindering the formation of ion pair.

Droplet volume

One of the important factors in SME, which has great influence on the extraction efficiency, is the volume of the microdrop. The influence of drop size was investigated in the range of 1-4 μl . It was found that the absorbance increases with drop volume in the range of 1-4 μl . When drop size exceeded 4 μl ,

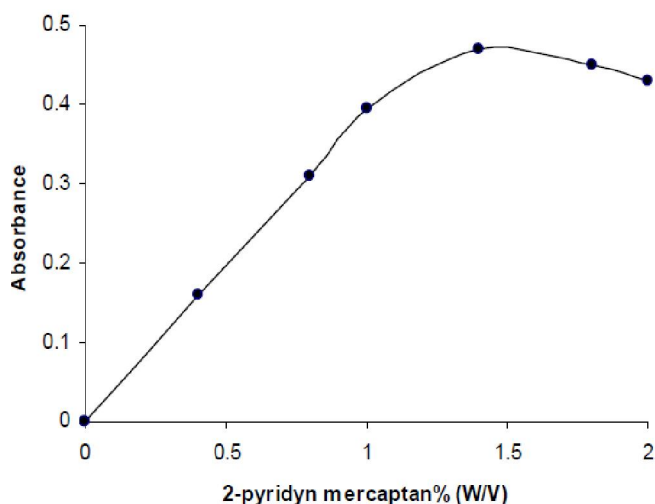


Figure 3 : Effect of concentration of 2-pyridyn mercaptan on the absorbance of cadmium obtained from SME

it became too unstable to be suspended at the needle tip. For this reason 4 μl drop volume was used for further studies.

Concentration of 2-pyridyn mercaptan

The influence of the concentration (0-2% w/v) of 2-pyridyn mercaptan (PyM) in the aqueous solution on the thallium cationic complex formation was investigated for 50 $\mu\text{g L}^{-1}$ solution of thallium under the optimum conditions described above and the results are shown in Figure 3. As can be seen in the Figure 3, the absorbance increases with increasing PyM concentration and its maximum value corresponds to 1.5% of PyM in the aqueous solution.

Concentration of picric acid

For the improving the extraction performance, ion pair complex was formed between $(\text{Tl}-\text{PyM})^+$ and $(\text{picrate})^-$. Different concentration (0-1%, w/v) of picrat were used. The results are shown in Figure 4, indicating that, the efficiency of thallium extraction increases with increasing the concentration of picric acid up to about 0.5 % and leveling off at higher concentration.

Stirring rate

Magnetic stirring was used to facilitate the mass transfer process and thus improving the extraction efficiency. The stirring rate was optimized for extraction process. The enrichment factor increased with increasing the stirring rate up to 500 rpm, because in high stirring rate a relatively large vortex

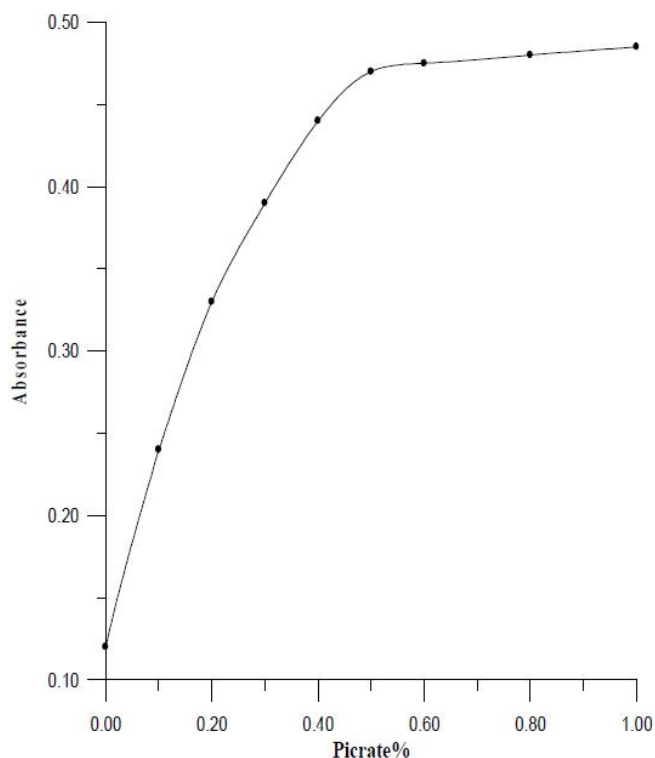


Figure 4 : Effect of concentration of picrate on the absorbance of cadmium obtained from SME

TABLE 1 : Interferences effect on the determination of $50 \mu\text{g L}^{-1}$, Tl(I)

Ion	Tolerance limit ($\mu\text{g L}^{-1}$)
$\text{S}_2\text{O}_8^{2-}$, MoO_4^{2-} , $\text{S}_2\text{O}_3^{2-}$, SeO_3^{2-}	200.0
Br^- , Cl^- , I^- , SCN^-	15.0
CH_3COO^- , NO_2^-	20.0
PO_4^{3-} , SO_4^{2-} , CO_3^{2-}	50.0
Hg^{2+} , Pb^{2+} , Cd^{2+}	1.5
Zn^{2+} , Fe^{2+} , Fe^{3+} , Sn^{2+} ,	50.0
Cu^{2+} , Cr^{3+} , Al^{3+} , Co^{2+} , Bi^{3+}	100.0
Na^+ , Li^+ , Ag^+ , Ca^{2+} , NH_4^+ , Ba^{2+} , K^+ , Mg^{2+}	200.0

is formed in the lower region of the organic solvent, but instability of droplet limited the phenomenon, thus 500 rpm was chosen for further experiments.

Extraction time

Extraction time is one of the most important factors in the most of extraction procedures. SME is a type of equilibrium extraction, and the optimal extraction efficiency is obtained when equilibrium is established. The time dependence for the extraction process was also investigated. All measurements were carried out with $50 \mu\text{g L}^{-1}$ of thallium under the optimized conditions. Figure 5 shows the absor-

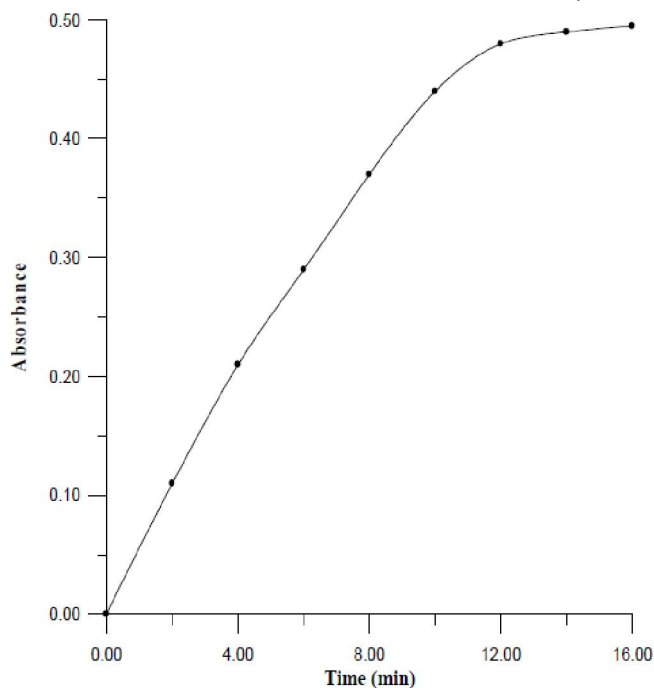


Figure 5 : Effect of extraction time on the absorbance of cadmium obtained from SME

bance of thallium versus extraction time. The results showed an increase of the thallium absorbance up to 12 minute and leveling off at higher extraction time. Therefore 12 minute was used as the optimum extraction time.

Interferences

The potential interference in the present method was investigated. The interference was due to the competition of other heavy metal ions for the chelating agent and their subsequent coextraction with thallium. Various salts and metal ions were added individually to a solution containing $50 \mu\text{g L}^{-1}$ of thallium, and the procedure was applied. The tolerance limit was set as the concentration of foreign substances required to cause a $\pm 5\%$ error. The results were shown in TABLE 1; clearly indicate that most of the tested ions do not interfere with preconcentration and determination of thallium. Thus, the selectivity of the proposed method is high enough to be used for determination of thallium ions in real samples.

Analytical figure of merits

Under the optimum conditions described above, the analytical performance characteristics of the proposed method are listed in TABLE 2. The enhancement factor was calculated as the ratio between the

TABLE 2 : Analytical characteristics of SME-FAAS for determination of thallium

Parameter	Analytical feature
Linear range ($\mu\text{g L}^{-1}$)	12-130
Correlation coefficient (r^2)	0.9989
Limit of detection ($\mu\text{g L}^{-1}$)(3σ , $n=10$)	3.6
Repeatability (RSD%) ($n=10$, $50 \mu\text{g L}^{-1}$)	4.9
Repeatability (RSD%) ($n=10$, $100 \mu\text{g L}^{-1}$)	4.7
Enrichment factor (EF)	188
Sample Volume (ml)	10
Microdrop volume (μl)	4
Sample introduction Volume (μl)	50
Sample preparation time (min)	12
Recovery (%)	94.0

TABLE 3 : Results (mean \pm standard deviation based on eight replicate analysis) of determination of thallium in reference materials and real samples

Reference Material	Certified value ($\mu\text{g g}^{-1}$)	Measured value ($\mu\text{g g}^{-1}$)	Recovery%
CRM 5406-90	45.8	43.5 ± 0.2	95.0
Sample	Thallium added ($\mu\text{g L}^{-1}$)	Thallium found ($\mu\text{g L}^{-1}$)	Recovery %
	-	<detection limit	-
Tap water ^a	40.0	39.0 ± 1.9	97.5
	80.0	79.4 ± 3.8	99.2
	-	<detection limit	-
Sea water ^b	40.0	39.3 ± 1.9	98.3
	80.0	81.0 ± 3.9	101.2
	-	<detection limit	-
Human plasma	40.0	40.2 ± 2.0	100.5
	80.0	82.0 ± 4.0	102.4

^a Sabzevar city, Iran, ^b collected at Caspian sea, Iran.

slopes of a curve established using aqueous solutions submitted to the solvent microextraction procedure and a curve with aqueous standards not submitted to this procedure and we could estimate a 188-fold enrichment factor for $50 \mu\text{l}$ sample which was introduced to the FAAS. The extraction recovery ($R\%$) was 94.0% which was calculated by equation (1).

$$R\% = (V_{\text{drop}} / V_{\text{solution}}) \times EF \times 100 \quad (1)$$

By considering the diluting factor, from $4 \mu\text{l}$ extracted drop to $50 \mu\text{l}$ introducing sample to the FAAS, the enrichment factor was equal to 2350.

A limit of detection of $3.6 \mu\text{g L}^{-1}$ was obtained for aqueous solutions (calculated as three times the standard deviation of the blank signal divided by the slope of the calibration plot). Relative standard deviation (RSD) for ten replicate measurement of

$50 \mu\text{g L}^{-1}$ and $100 \mu\text{g L}^{-1}$ thallium was 4.9 % and 4.7%, respectively. The calibration graph was linear in the range of $12-130 \mu\text{g L}^{-1}$ with correlation coefficient of 0.9989 under the optimum conditions of the recommended procedure.

Application

In order to establish the accuracy of the proposed method, the method has been applied to the determination of thallium in certified reference alloy (CRM 5406-90). Using the standard addition technique, a recovery of 95.0% was achieved. The amount of thallium found (43.5 ± 0.2) well agreed with the certified value ($45.8 \mu\text{g g}^{-1}$).

To show the applicability of the method, human plasma, local tap water and sea water were analysed for its thallium content. Plasma of two miner volun-

teer, who worked in zinc mine were chosen as real sample. The blood samples centrifuged and plasma was separated and stored in -20 °C. The amount of thallium was analysed by proposed method. The results obtained are presented in TABLE 3.

CONCLUSIONS

A method of ion pair solvent microextraction (IP-SME) coupled to FAAS has been developed for the sensitive determination of thallium in aqueous samples and human plasma. Good preconcentration was obtained easily through this method and low detection limit was achieved with only 10 ml of sample. Apart from having extremely high sensitivity, the procedure is very simple, nearly fast and benefits a very low detection limit. By the use a preliminary separation step using a resin, the method could be relatively free from interferences. The experimental parameter such as type and volume of organic solvent, pH, concentration of chelating agent and counter ion, extraction time and stirring rate have great effects on the sensitivity of method and should be optimized.

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