Preconcentration of thallium (I) by single drop microextraction with electrothermal atomic absorption spectroscopy detection using dicyclohexano-18-crown-6 as extractant system

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ABSTRACT

A simple single drop liquid-phase microextraction (SDME) technique, combined with electrothermal atomic absorption spectroscopy (ETAAS) is developed both to preconcentrate and determine thallium (I) ions in aqueous solutions. The ions were transferred from 10.0 ml of aqueous sample (donor phase) containing 0.5 ml of 1% picric acid as the ion-pair agent into a 3 μl microdrop of nitrobenzene (acceptor phase) containing dicyclohexano-18-crown-6 as the complexing agent. The latter will help to improve the extraction efficiency of the analyte. After the ions have been extracted, the acceptor drop was directly injected into a graphite furnace for thallium (I) determination. Several parameters such as the extracting solvent, extraction time, temperature, concentration of picric acid and crown ether, drop volume and stirring rate were examined. Under the optimized experimental conditions, the detection limit (L.O.D.) was 0.7 ng ml^{-1}. The relative standard deviation for five replicate analysis of 10 ng ml^{-1} of thallium (I) was 5.1%. The calibration curve was linear in the range of 3–22 ng ml^{-1}. The results for determination of thallium in reference material, spiked tap water and seawater demonstrated the accuracy, recovery and applicability of the presented method. The enrichment factor was 50.

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1. Introduction

The determination of Tl (I) is of great interest because of its clinical and environmental roles and also industrial applications [1–4]. Tl (I) is highly toxic to the biosphere even more than Hg, Cd, Pb and Cu [5,6]. Tl is known to have mutagenic, carcinogenic and teratogenic effects [7]. 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} [8] whereas in non-polluted soils lies typically between 0.3 and 0.55 mg kg^{-1} [9]. However the determination of low concentration of thallium (I) in environmental samples will call for a highly sensitive technique.

A recent review, by Das et al. [10], on the determination of thallium at ultra-trace level in aqueous solutions illustrates the developments of preconcentration techniques and sensitive detection methods. The separation of thallium (I) has been intensively studied through the formation of ion-pair complex with basic triphenymethane dye [11], with cryptand 2,2,2, erythrosine [12] and benzo-15-crown-5 [13], 18-crown-6 [14] and dibenzo-24-crown-8 [15] or 12-crown-4 [16] with picrate. The complexation reaction

between Tl (I) and crown ethers in organic solvents at 25 °C with stoichiometry of 1:1 has been studied and the best crown ether was found to be DCH-18-crown-6 [17].

Many microextraction techniques such as solid-phase microextraction (SPME) for aqueous samples have been used recently [18,19]. Although these techniques do not need any solvent, they suffer from memory effects [20]. Liquid-phase microextraction (LPME) technique in which the acceptor phase in the form of a drop of an organic solvent built up at the tip of a syringe and surrounded by an aqueous solution of a sample (donor phase) has been described by Jeannot and Cantwell [21,22]. This method (in contrast to LLE and SPE), avoids high solvent consumption and does not involve the fiber problem (in contrast to SPME) [23,24]. This method can be also quick and inexpensive.

In 2003, Chamsaz et al. [25] reported a preliminary study on the combination of headspace sampling-single drop liquid-phase microextraction (HS-SDME) with electrothermal atomic absorption spectroscopy (ETAAS) for the analysis of inorganic compounds. HS-SDME was demonstrated to be an efficient extraction technique for analyzing arsenic in real samples like tap water and washing-machine powder. Recently, Hu and co-workers [26] reported that the implementation of SDME in trace-element analysis could give rise to another important field of applications. Few analytical applications of the SDME method for the extrac-

tion and preconcentration of metal ions have been reported [27–29].

The present work describes a rather simple method for extraction, preconcentration and determination of thallium (I) based on LPME complemented by graphite furnace atomic absorption spectrometry. The results indicate that LPME possesses a good preconcentration factor, sensitivity, and low detection limit; therefore it could be considered as an efficient technique for analysis of thallium (I) in real samples such as tap water. Procedural parameters such as the organic solvent, extraction time, stirring rate and the concentration of dicyclohexano-18-crown-6 affecting the extraction efficiency were investigated. The present work was led to a fast, simple and relatively high sensitive technique for determination of thallium (I) in aqueous samples.

2. Experimental

2.1. Apparatus

A 10 μl microsyringe (Hamilton) was used both to keep the drop of the acceptor phase and inject it into the graphite furnace atomizer. A sampler (ependorf, Germany) was applied to inject the modifier solution into the graphite tube. An F20520162 VELP SCIENTIFICA magnetic stirrer (Italia) was employed to stir the sample solution.

A shimadzu model AA-670 atomic absorption spectrometer with GFA-4B graphite furnace atomizer with a D_2 lamp for the background correction was used.

A thallium hollow cathode lamp, adjusted at 5 mA, was used as the radiation source. Measurements were carried out in peak high mode at 276.8 nm, using a spectral bandwidth of 0.5 nm. The atomic absorption signal at 276.8 nm was recorded on a graphic printed PR-4, and the height of the peak was used for determination of thallium. The temperature program for the furnace is given in Table 1.

2.2. Reagents

All reagents were of analytical reagent grade and triply distilled water was used throughout. A stock solution of $1000 \, mg \, L^{-1}$ thallium (I) ion was prepared by dissolving the appropriate amounts of thallium nitrate (Merck, Darmstadt Germany) in 1% HNO_3. Working standard solutions were prepared freshly at various concentrations by diluting the stock standard solution with distilled water. A 1% (m/v) picric acid (Wako Pure Chemicals) solution was prepared acting as the counter ion. The acceptor organic phase was nitrobenzene (Analar) containing a fixed amount of 2% (m/v) dicyclohexano-18-crown-6 (Flucka) as the complexing agent. The stock standard solution of Pd ($1 \, g \, L^{-1}$) was prepared by dissolving $Pd(NO_3)_2$ (Merck) in diluted nitric acid. The following reagents were employed for studying interference effects:

KNO_3, $NaNO_3$, $Mg(NO_3)_2 \cdot 6H_2O$, $Ca(NO_3)_2 \cdot 4H_2O$, $AgNO_3$, $Zn(NO_3)_2 \cdot 6H_2O$, $Fe(NO_3)_3 \cdot 9H_2O$, $Pb(NO_3)_2$, $Cd(NO_3)_2 \cdot 4H_2O$, $Ba(NO_3)_2$, $Cu(NO_3)_2 \cdot 3H_2O$, $Ni(NO_3)_2 \cdot 6H_2O$, NH_4NO_3, $Hg(NO_3)_2 \cdot H_2O$, NaCl, NaF and $NaNO_3$ all from Merck.

Table 1
GFA heating program.

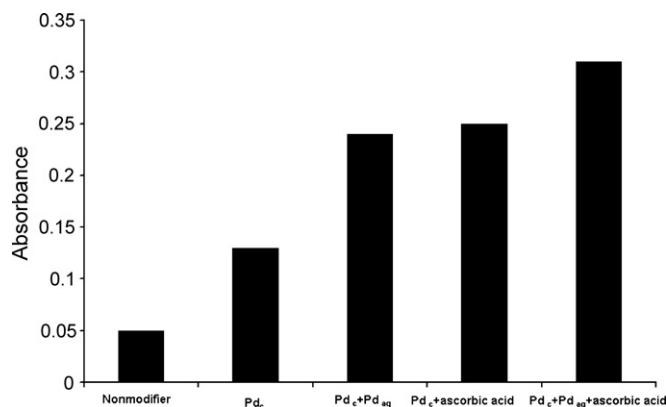| Stage	Furnace temperature (°C)	Mode	Time (s)	Ar flow rate (L min^{-1})
Drying	120	Ramp	10	1.5
Ashing	300	Step	15	1.5
Atomization	1900	Step	3	0 (gas stop)
Cleaning up	2500	Step	2	1.5

Fig. 1. The effect of different modifiers for thallium signal.

2.3. Analysis procedure

Several modifiers were tested for efficient thermal stabilization of thallium such as Pd (80 μg), ascorbic acid (200 μg), and Pd mixture with ascorbic acid (80 μg Pd + 200 μg ascorbic acid). As can be seen in Fig. 1. Pd deposited (Pd_c) on the tube wall + $Pd_{(aq)}$ + ascorbic acid$_{(aq)}$ was shown to be superior and chosen as an efficient modifier. Graphite tubes were pretreated using 40 μl of 0.1% Pd solution injected into the tubes and conditioned at a temperature of 1800 °C. This procedure was repeated two times, resulting in a total mass of 80 μg of Pd deposited (Pd_c) on the tube wall. The sample and modifier solutions containing 20 μl of Pd^{2+} (0.1%, w/v) and 20 μl of ascorbic acid (1% w/v) were subsequently injected into the graphite furnace. This modifier system shows low detection limits, high sensitivity and long lifetime.

0.5 ml of 1% picric acid, as a counter ion, was added to 10 ml of the sample solution containing thallium (I). The solution was stirred by a magnetic stirrer with a 6-mm bar at an optimized speed of 500 rpm. The ion-pair, $Tl^+picrate^-$, formed were extracted by the acceptor phase consisting 3 μl of nitrobenzene for 20 min at 25 °C. The 3 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 directly injected into the graphite furnace for subsequent determination. The parameters affecting the complexation and extraction efficiency were optimized.

3. Results and discussion

3.1. Optimization of liquid-phase microextraction

It is essential to optimize all the parameters affecting the performance of liquid-phase microextraction of Tl (I) from the aqueous samples. These parameters consist of organic solvent type, pH, stirring rate, concentrations of crown ether and picric acid, volume of aqueous and organic phase, the sampling temperature and the extraction time. All measurements were carried out with an aqueous solution containing 20 ng ml^{-1} of Tl (I). The effects of each parameter on the extraction process were examined and the results are as follows.

3.1.1. Solvent type

The selection of an appropriate extracting solvent is very important for SDME. Four solvents, i.e., carbon tetrachloride, chloroform, dichloromethane and nitrobenzene were tested for the extraction of Tl (I) from 10 ml of 20 ng ml^{-1} solution at pH value of 3. The extraction of thallium was performed using 3 μl of an appropriate
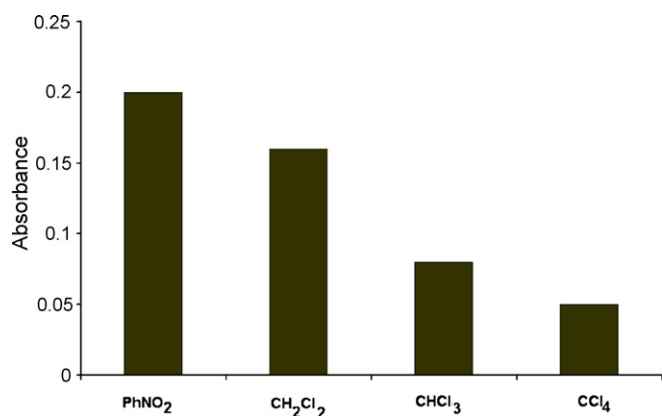
Fig. 2. The influence of solvent type on Tl (I) extraction.

Fig. 4. The effect of DCH-18-crown-6 concentration on Tl (I) extraction

organic solvent and stirring (500 rpm) the sample for 5 min. The final results are presented in Fig. 2.

The experimental results demonstrated that nitrobenzene provided higher extraction efficiency than other organic solvents. This may be attributed to the greater polarity of nitrobenzene relative to other solvents, leading to a higher solubility towards the ionic [(DCH-18-crown-6 Tl)]$^{+}$ complex and therefore higher extraction efficiency.

3.1.2. pH

The effect of sample pH on the extraction of thallium complex was studied. Other experimental conditions were as follows: 20 ng ml^{-1} Tl; stirring rate of 500 rpm; 3 μl drop volume; 10 ml sample volume; 0.2% DCH-18-crown-6. The results are shown in Fig. 3. The best pH for extraction of Tl (I) was found to be around 5. The pH of the primary solution of Tl with picric acid was 3. The absorbance was increased at a pH value around 5 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. The buffer containing acetic acid/acetate solution (0.1 M) adjusted at this pH value was used for further experiments.

3.1.3. Stirring rate

Magnetic stirring was used to facilitate the mass-transfer process and thus improving the extraction efficiency. The stirring rate was optimized for the extraction process. The enrichment factor increased with increasing the stirring rates up to 500 rpm. At higher rates, however, the droplet would become unstable and hence 500 rpm was chosen for further experiments.
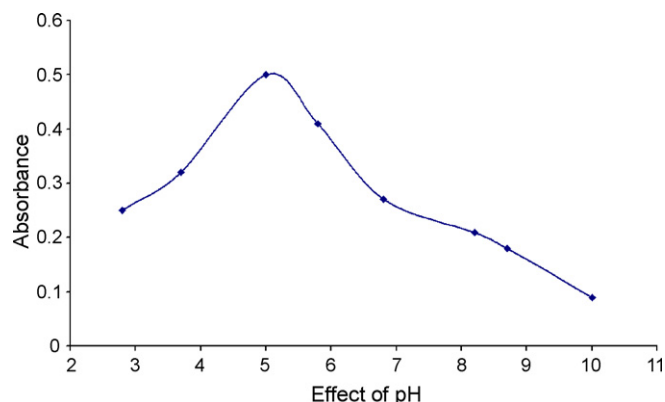
3.1.4. Concentration of DCH-18-crown-6

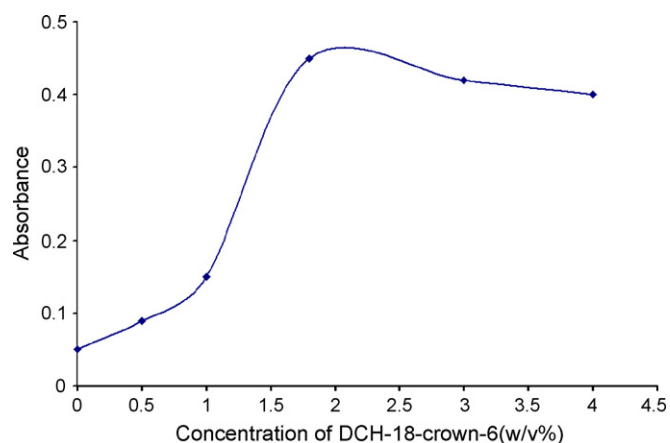Different amounts of DCH-18-crown-6 were added to the organic solvent making a range of concentrations between 0 and 4% (w/v). Under the optimum conditions described above, the effects of DCH-18-crown-6 concentration on the extraction efficiency is shown in Fig. 4. The enrichment factor increases with increasing DCH-18-crown-6 concentration and its maximum value corresponds to 2% of DCH-18-crown-6 in the drop.

3.1.5. Concentration of picric acid

The effect of picric acid on the ion-pair formation of thallium (I), in the donor phase, for improving the extracting performance of the technique was investigated. The extraction was carried on for 10 min. Different concentrations (0–0.1%, w/v) of picric acid were used. The results are shown in Fig. 5, indicating that, the efficiency of thallium transport increases with increasing the concentration of picric acid up to about 0.06% and then decreases with increasing its concentration. This may be due to the competition of picric acid itself with ion pair for transport through the organic phase of the single drop. Therefore, 0.06% was employed as the optimum concentration of picric acid.

3.1.6. Volume of aqueous and organic phase

The influence of the organic drop phase volume was studied in the range of 1–3 μl. The results show that increasing the volume of organic phase increases the extraction efficiency. Higher volumes were avoided due to mechanical instability of the drop. Therefore 3 μl drop volume was used for further studies.

The varying volumes of the sample solution were tested and 10 ml of the sample solution was chosen for the analysis. Lower vol-
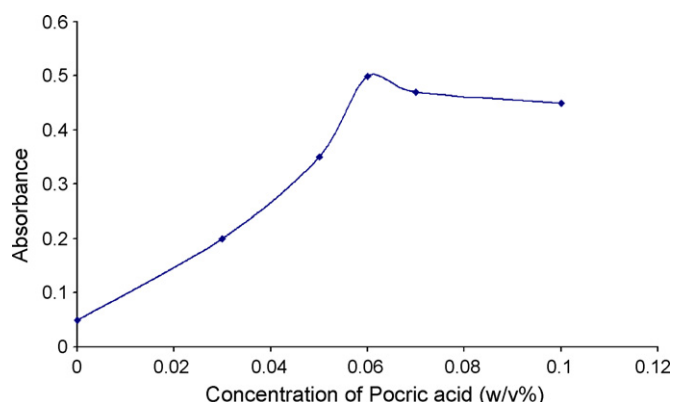

Fig. 3. The effect of pH on Tl (I) extraction.

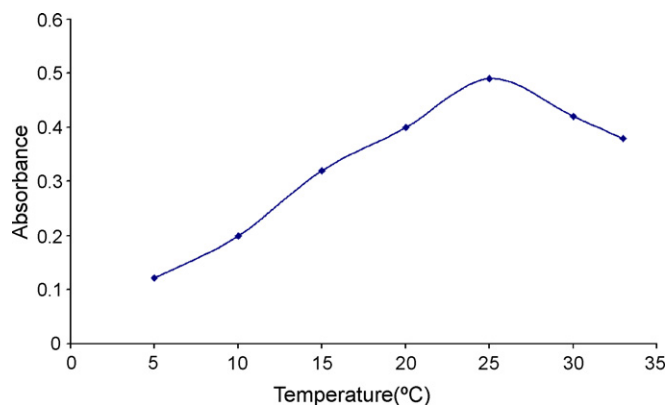**Fig. 5.** The effect of picric acid concentration on Tl (I) extraction.

Fig. 6. The effect of temperature on Tl (I) extraction.

umes caused falling off the drop under agitation and higher volumes showed no benefit to the extraction process.

3.1.7. Temperature

The effect of sample temperature was studied in the range of 5–35 °C while keeping the drop in the aqueous solution for 10 min.

The corresponding curve (Fig. 6) shows that the efficiency of extraction increases with increasing of the temperature up to 25 °C and then decreases significantly at higher temperatures due to the thermal instability of the extracting solvent. Therefore, the optimum sampling temperature was selected to be 25 °C.

3.1.8. Extraction time

The time dependence for the extraction process was also investigated. All measurements were carried out with $10\,ng\,ml^{-1}$ of Tl (I) under the optimized conditions. The results show an increase of thallium absorbance up to 20 min and leveling off at higher extraction times. This may be due to the dissolution of nitrobenzene in aqueous phase and gradual reduction of drop volume with time. Therefore the optimum extraction time was taken to be 20 min as shown in Fig. 7.

3.2. Interference effects and eliminate

Interfering species at 100-fold excess were added to Tl (I) solution and the extraction procedure was followed. The results of interference effects as the average relative percentage error are shown in Table 2. The severe interferences were due to F^-, Cl^-, Ba^{2+}, Sb^{3+}, Pb^{2+}, Cd^{2+}, K^+, Ag^+, Fe^{3+}, Mg^{2+}, Zn^{2+} and Ca^{2+}.
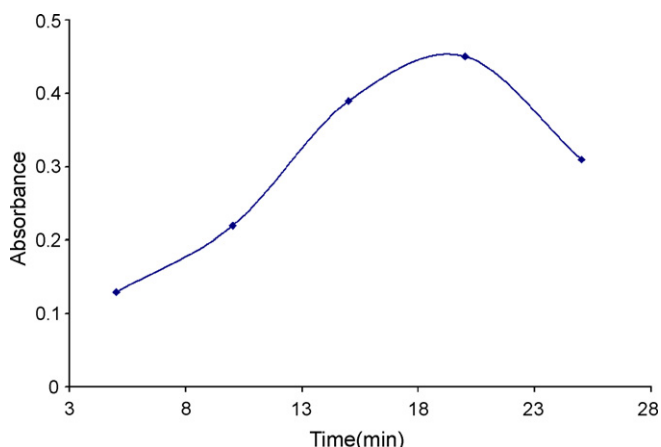

Fig. 7. The effect of extraction time on Tl (I) preconcentration.

Table 2
Effect of interferences on determination of $10\,ng\,ml^{-1}$ thallium in the presence of 100-fold of foreign ions.

Interfering ion	Relative absorbance[a]	Relative absorbance after interference elimination
K^+	1.51	–
Na^+	1.00	–
Mg^{2+}	1.24	1.00
Ca^{2+}	1.47	1.05
Ag^+	1.50	1.14
Zn^{2+}	1.51	1.10
Fe^{3+}	1.40	1.04
Pb^{2+}	1.57	1.03
Cd^{2+}	1.61	1.09
Ba^{2+}	1.37	1.07
Sb^{3+}	1.17	1.06
Cu^{2+}	1.10	–
Ni^{2+}	1.06	–
NH_4^+	1.10	–
Hg^{2+}	1.09	–
Cl^-	1.63	1.03
F^-	1.60	1.00
NO_3^-	1.06	–

[a] The relative absorbance is defined as: relative absorbance = (absorbance of $10\,ng\,ml^{-1}$ thallium + foreign ion $1000\,ng\,ml^{-1}$)/absorbance of $10\,ng\,ml^{-1}$ thallium. All results are the average of triplicate measurements.

The results show that EDTA at a concentration of 0.005 M could be used as a masking agent for removing the interference effects of different metal ions studied without affecting the Tl (I) absorbance because it does not form any complex with EDTA at pH 5. A column was prepared with 5 g Amberlite resin (IRA-400) for removal of anions (F^- and Cl^-). The results show that by passing the solution into the column, all of the anions were removed and Tl content of the solution showed no interference effect. After removal of interfering ions, the relative error decreased to the amounts shown in Table 2.

3.3. Analytical figures of merit

A calibration curve was obtained using 10 ml of thallium solution treated at the optimized conditions. The calibration curve was linear in the range of 3–$22\,ng\,ml^{-1}$ Tl (I). The calibration equation was $A = 0.0523C - 0.06$ with a correlation coefficient of 0.998, where C was the concentration of Tl^+ in $ng\,ml^{-1}$. The detection limit, calculated according to three times of the standard deviation of the blank signal after the preconcentration step was $0.7\,ng\,ml^{-1}$. The relative standard deviation (R.S.D.) for five replicate analyses of $10\,ng\,ml^{-1}$ thallium was 5.1%. The concentration factor defined as the concentration ratio of thallium in the microdrop to that of the initial solution was 50. For calculating the enrichment factor, a 50-$ng\,ml^{-1}$ solution of thallium was directly injected into the graphite furnace and its absorbance was measured. The same solution was then analysed by the present method, and after appropriate dilution was injected into the graphite furnace and its absorbance was measured. By comparing the two absorbances, the enrichment factor was calculated.

3.4. Analysis of real sample

In order to evaluate the accuracy and recovery of the proposed method, a standard rock reference material, NCSDC 73301, obtained from the geological survey of Japan was analysed for its thallium content. The rock sample (0.5 g) was dissolved in a mixture of HF (500 ml), HNO_3 (45 ml) and H_2SO_4 (165 ml) in a Teflon beaker, and heated until 2 ml of solution was remained. To this solution concentrated HNO_3 (8 ml) was added and after heating treated with distilled water was added to give a clear solution and was finally

Table 3
Results (mean ± standard deviation based on five replicate analysis) of determination of thallium in water sample.

Sample	Thallium added (ng ml⁻¹)	Thallium found (ng ml⁻¹)	Recovery (%)
Tap water[a]	0	3.5 ± 0.3	–
	5	8.2 ± 0.3	94
	10	13.1 ± 0.2	96
Seawater[b]	–	9.6 ± 0.5	–

[a] Mashhad city, Iran.
[b] Collected at Caspian Sea, Babolsar, Iran.

made to 100 ml by further addition of distilled water. This solution was analysed for its Tl content according to the proposed procedure and was determined to be $1.75 \pm 0.25 \, \mu g/g$ which is in good agreement with its certified value ($1.93 \pm 0.55 \, \mu g/g$) with a recovery of 91%. Spiked Tl solutions at 5 and 10 ng ml⁻¹ concentrations into the tap water were also conducted in order to measure the extraction efficiency. Each experiment was repeated for five times and the recoveries given in Table 3 are the mean of five calculations. The recovery for the method was calculated to be in the range of 91–96%. Thallium in tap water and seawater samples were also determined in order to show the applicability of the method. The results are given in Table 3.

4. Conclusion

The results show a promising technique for determination of trace amounts of thallium (I) in water samples without the need for any sophisticated device. In addition to its relatively high sensitivity, the procedure is simple, and benefits a low detection limit. By the use of a preliminary separation step using Amberlite resin (IRA-400) for removal of anions and EDTA (0.005 M) for masking the metal ions, the method becomes relatively free from interferences. Each of the experimental parameters i.e., organic solvent type, pH of aqueous phase, sampling temperature, extraction time and volume of the aqueous and organic phase has a great effect on the sensitivity of the method and should be optimized.

The results show that Tl (I) could be determined with relatively high sensitivity and relatively a good reproducibility in aqueous samples such as tap water and seawater, as well as in solid sample such as soils and rocks.

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