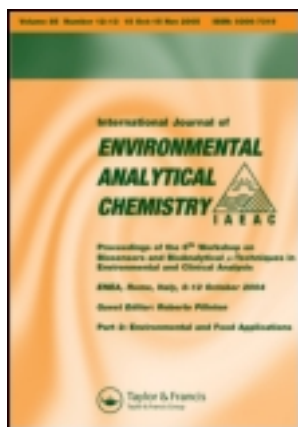


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Determination trace amounts of thallium after separation and preconcentration onto nanoclay loaded with 1-(2-pyridylazo)-2-naphthol as a new sorbent

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A procedure has been proposed for the separation and preconcentration of trace amounts of thallium. It is based on the adsorption of thallium ions onto organo nanoclay loaded with 1-(2-pyridylazo)-2-naphthol (PAN). Thallium ions were quantitatively retained on the column in the pH range of 3.5–6.0, whereas quantitative desorption occurs with 5.0 mL of 5% ascorbic acid and thallium was determined by flame atomic absorption spectrometry. Linearity was maintained between 0.66 ng mL^{-1} – $15.0 \text{ } \mu\text{g mL}^{-1}$ in initial solution. Detection limit was 0.2 ng mL^{-1} in initial solution and preconcentration factor was 150. Eight replicate determinations of $2.0 \text{ } \mu\text{g mL}^{-1}$ of thallium in final solution gave a relative standard deviation of $\pm 1.48\%$. Various parameters have been studied, such as the effect of pH, breakthrough volume and interference of a large number of anions and cations and the proposed method was used to determine thallium ions in water and standard samples. Determination of thallium ions in standard sample showed that the proposed method has good accuracy.

Keywords: nanoclay; preconcentration; thallium determination; solid phase extraction

1. Introduction

In recent years, great attention has been paid to the application of nano structure materials. Since clay and clay minerals have primary particles with at least one dimension in the nanometer scale, they may be regarded as nanomaterials of geological and pedological origins [1]. Montmorillonite is an important class of clay minerals because of its specific properties such as a high cation exchange capacity, adsorption, high surface area and swelling behaviour [2]. The elementary layers of montmorillonite are a few hundred nanometers in length and width and about 1 nm in thickness [3]. Clays could be modified with the physical and chemical modifications such as acid activation, thermal treatment and adsorption and intercalation of small and polymeric organic species [4]. Clay minerals can react with different types of organic compounds in particular ways. Alkylammonium ions, in industrial applications mainly quaternary alkylammonium ions, are widely used in modifying montmorillonite [5]. Microporous materials were obtained by replacing the interlayer exchangeable cations in montmorillonite with

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tetraalkylammonium ions. The synthesis of the first organic pillared clay minerals with an interlayer distance of 0.5–0.6 nm and a permanent porosity was reported [6]. Normally, organic surfactants are used to make the surface of clay platelets organophilic [7].

Thallium is one of the rare elements of the earth's crust. Thallium is a non-essential toxic element with no known beneficial biological role, which has various industrial applications such as semiconductors, nuclear medicine, catalysts, dyes and pigments, thereby increasing the risk of occupational poisoning and environmental pollution [8]. Thallium is also used in medicine, rodenticides and insecticides [9]. Both the element and its compounds are extremely toxic; skin-contact, ingestion and inhalation are all dangerous. By exploiting and machining minerals, thallium enters and contaminates the environment. Therefore, it is important to remove trace amounts of thallium and strictly control its occurrence in order to prevent harm to humans and the environment [10]. The determination of thallium in environmental samples is of interest because of the high toxicity of its compounds. Due to new concerns regarding the toxicity of thallium, there is a growing need for improved analytical methods for monitoring this metal [11]. Thallium determination in the environmental samples is a very difficult task because of its low concentration levels and interference effects [12]. One way to solve this problem is separation and preconcentration of the ion of interest in order to enhance the detection limit and selectivity and thereby improve the precision and accuracy of analytical results. Solid phase extraction (SPE) is one of several procedure techniques which are used for this purpose [13]. The nano-size dimension, extensive surface area and peculiar charge characteristics of nanoclay materials lie behind their large propensity for taking up ions and organic compounds [14]. Therefore, nanoclay may be suitable for preconcentration in solid phase extraction. The aim of the present investigation is to investigate the potential of nanoclay for preconcentration and develop a sorbent for separation of trace amounts of thallium ions. The present work reports the application of organo nanoclay loaded with 1-(2-pyridylazo)-2-naphthol as an easily prepared and stable solid sorbent for preconcentration of trace amounts of Tl ions in an aqueous solution. In the present work, a simple, sensitive and economical method is developed for FAAS determination of trace amounts of Tl ions after separation and preconcentration onto PAN loaded modified nanoclay as sorbent.

2. Experimental

2.1 Instruments

A Varian model SpectrAA 220 flame atomic absorption spectrophotometer (Varian, Australia) was used for measuring Tl, in air-acetylene flame under the conditions that were set as recommended by the manufacturer, in the following conditions: wavelength: 276.8 nm, lamp current: 10 mA, slit width: 0.5 nm, acetylene flow: 1.5 L min⁻¹, air flow: 3.5 L min⁻¹. The pH measurement was carried out using a Metrohm pH meter (Model 713) with a combined pH glass electrode calibrated against two standard buffer solutions at pH 4.0 and 7.0. A funnel-tipped glass tube (80 × 10 mm) was used as a column for preconcentration. All glassware and columns were washed with a mixture of concentrated hydrochloric acid and concentrated nitric acid (1 : 1) before use.

2.2 Reagents

All chemicals were of analytical-reagent grade and were provided by Merck (Darmstadt, Germany) and all solutions were made up with ultra-pure quality water, which was

produced by a Milli-Q system (Millipore Bedford, USA). A standard thallium solution was prepared from thallium (I) nitrate in a minimum volume of concentrated nitric acid and then diluted to 1000.0 mL with distilled water in a standard flask and standardised by a known method [15]. A 0.05% solution of PAN in ethanol was prepared. Buffer solutions of pH 3–6 and 6–7.5 were prepared by mixing appropriate ratios of a 0.2 M acetic acid and 0.2 M sodium acetate solution and 0.1 M sodium dihydrogen phosphate solution and 0.1 M disodium hydrogen phosphate solution, respectively. The nanoclay particles were organically modified montmorillonite in a platelet form, i.e. 10 μm long, 1 μm wide and 50 nm thick, called Nanomer I30E from Nanocor.

2.3 Preparation of PAN loaded modified nanoclay

Industrial purified commercial modified montmorillonite was heated to 50°C, and then was dispersed in the 0.05 solution of PAN in ethanol at room temperature, with vigorous stirring for 8 h for adsorption of PAN onto nanoclay. The sample was filtered, washed and then dried at 60°C and stored until use.

2.4 Column preparation

A quantity of 300 mg of PAN loaded modified nanoclay was dispersed in water, and then poured into a funnel-tipped glass tube plugged with a small piece of glass wool at the ends. A glass column packed with 300 mg of PAN loaded modified nanoclay sorbent was used as the operational column for preconcentration. Before sample loading the column must be preconditioned by passing a buffer solution. The column could be used repeatedly for 20 times at least.

2.5 General procedure

An aliquot of thallium solution (containing 0.5 to 75.0 μg) was placed in a 50 mL beaker and 2 mL of acetate buffer solution with pH 5.1 was added to it, then diluted to \sim 40 mL with distilled de-ionised water. This solution was passed through the column at a flow rate of 4 mL min^{-1} . After the passing of this solution, the column was washed with 5 mL of distilled de-ionised water. Adsorbed Tl ions on the column were eluted with 5.0 mL of 5% ascorbic acid solution at a flow rate of 2 mL min^{-1} . The eluent was collected in a 5.0 mL volumetric flask and thallium was determined by flame atomic absorption spectrometry against the blank prepared in the same manner without the addition of thallium ions.

3. Results and discussion

Preliminary experiments showed that although Nanomer I30E organo nanoclay has a low tendency for retention of Tl adsorption (less than 60%), it is not selective for separation of thallium. Therefore, the Nanomer I30E nanoclay is not considered as a suitable sorbent for separation of thallium ions. However, recent work [16] indicates that nanoclay can adsorb organic materials. So, the PAN was added to organo nanoclay, and then the PAN immobilised organo nanoclay was studied for separation and preconcentration of Tl. The results showed that the recovery of thallium ions by using Nanomer I30E nanoclay is higher than 96%. Moreover, Nanomer I30E nanoclay is selective for separation Tl ions.

In order to obtain highly sensitive, accurate and reproducible results, analytical parameters including pH, type and volume of eluent solution and breakthrough volume were optimised for preconcentration of Tl ions.

3.1 Reaction conditions

The reaction conditions were investigated with 10.0 μg of thallium ion. The percentage sorption of thallium ion was examined on the sorbent surface as a function of the pH sample solution in the range of 2.0–7.5. The pH was adjusted by using acetate buffer solution. The percentage recovery of Tl ions depends on the pH of the sample solution, and is higher than 97% in the pH range 3.5–6.0; therefore in subsequent studies, the pH was maintained at approximately 5.1. In the pH range 3.5–6.0, thallium ions could chelate with 1-(2-pyridylazo)-2-naphthol immobilised on nanoclay sorbent, and therefore be retained in the column.

The flow rate of sample solution was varied from 0.5–6 mL min^{-1} . It was found that a flow rate of 0.1–5 mL min^{-1} did not affect the recovery of thallium ion; therefore a flow rate of 4 mL min^{-1} was recommended in all experiments. The flow rate of eluent solution was varied from 0.5 to 5 mL min^{-1} . It was found that a flow rate of 0.5–3 mL min^{-1} did not affect recovery of thallium ion; therefore a flow rate of 2 mL min^{-1} was recommended in all experiments.

Keeping the other variables constant, the volume of the aqueous phase was varied in the range of 50–850 mL under the optimum conditions. It was observed that the thallium recovery was almost constant up to 750 mL (preconcentration factor 150). However, for convenience, all the experiments were carried out with 40 mL of the aqueous phase. Preliminary observations indicated that thallium was desorbed completely from sorbent with 5.0 mL of 5% ascorbic acid; therefore it was used in the present work. The ascorbic acid eluent can disrupt the formed Tl-PAN complex and elute thallium ions from the column.

3.2 Evaluation of sorbent property

The sorption capacity of PAN loaded modified nanoclay was determined by passing 50 mL of 60 $\mu\text{g mL}^{-1}$ Tl ions, followed by the determination of retained Tl ions using FAAS. The maximum capacity of the sorbent was 2.5 mg of Tl per gram of sorbent. The PAN loaded modified nanoclay sorbent was subjected to several loadings with the sample solution and subsequent elution. It was found that the adsorption properties of the adsorbent remained constant after 20 cycles of sorption and desorption.

3.3 Calibration curve and sensitivity

The calibration curve was evaluated for the determination of thallium according to the recommended procedure under the optimised conditions. Under optimum conditions, the calibration curve was linear from 0.66 ng mL^{-1} to 15.0 $\mu\text{g mL}^{-1}$ in initial solution or 0.1 to 15.0 $\mu\text{g mL}^{-1}$ in final solution. The equation of the calibration curve obtained after analysis of the eluent using FAAS was $A = 0.02C + 0.002$, with $R^2 = 0.9991$, where A is the absorbance value of the eluent and C is the concentration of Tl ($\mu\text{g mL}^{-1}$) after preconcentration. The recommended procedure was repeated eight times to find the

relative standard deviation in the determination of $2.0 \mu\text{g mL}^{-1}$ of Tl ion. RSD was found to be 1.48%. The obtained limit of detection was 0.2 ng mL^{-1} based on three times the standard deviation of the blank solution measurements ($n=8$) in original solution.

3.4 Interferences

Various ions were added individually to a solution containing $10.0 \mu\text{g}$ of thallium and the general procedure was applied. The tolerance limit was set as the concentration of the diverse ion required to cause $\pm 4\%$ error in the determination of thallium. The results obtained are given in Table 1. Among the examined ions, most of them could be tolerated up to milligram levels except EDTA. Table 1 shows the results. Thus the proposed method is relatively selective and can be used for the determination of thallium in different samples.

3.5 Analysis the pepperbush NIES sample

A 200 mg amount of pepperbush reference material (NIES No. 1) sample was decomposed with 5 mL of a mixture containing nitric and hydrochloric acid (1:1 ratio); and the solution was evaporated to dryness on a water-bath. This process was repeated twice, and 10 mL of distilled de-ionised water was added to the residue. The suspension was filtered through a filter paper circle blue ribbon, and a preconcentration procedure was applied to the final solution. The results are given in Table 2 which has good agreement with the certified value.

Table 1. Effect of interference.

Ion	Tolerance limit, mg
CH_3COO^- , NO_3^-	1000
SO_4^{2-}	195
I^- , F^-	200
Cl^- , CO_3^{2-}	85
Thiourea, SCN^-	25
EDTA	0.2
Mg^{2+}	145
Ca^{2+}	95
Cd^{2+} , Pb^{2+}	40
Sb^{3+}	15
Zn^{2+} , Ni^{2+}	2
Bi^{3+} , Co^{2+}	5
Mn^{2+} , Mo^{6+} , As^{3+}	8
Hg^{2+}	2.7
Fe^{3+}	1.3

Conditions: Tl, $10.0 \mu\text{g}$; flow rate of sample, 4 mL min^{-1} ; eluent solution, 5.0 mL of 5% ascorbic acid with flow rate 2 mL min^{-1} ; instrumental setting: wavelength, 276.8 nm ; lamp current, 10 mA ; slit width, 0.5 nm ; acetylene flow, 1.5 L min^{-1} ; air flow as oxidant, 3.5 L min^{-1} .

Table 2. Determination of thallium in standard pepperbush sample. Conditions and instrumental setting were same as Table 1.

Sample	Composition	Found* ($\mu\text{g g}^{-1}$)	Recovery (%)
NIES, No. 1 Pepperbush	K, 1.51 ± 0.06 ; Mn, 0.203 ± 0.17 ; Mg, 0.408 ± 0.020 ; Ca, 1.38 ± 0.07 % Cd, 6.7 ± 0.5 ; Ni, 8.7 ± 0.6 ; Fe, 205 ± 17 ; Co, 23 ± 3 ; Pb, 5.5 ± 0.8 ; Cu, 12 ± 1 ; Zn, 340 ± 20 ; Ba, 165 ± 10 ; Na, 106 ± 13 ; Rb, 75 ± 4 ; Sr, 36 ± 4 ; As, 2.3 ± 0.3 ; P, 1100; Cr, 1.3; Cs, 1.2; Hg, 0.05; Tl, $0.13 \mu\text{g g}^{-1}$	0.128 ± 0.003	98.46

Notes: NIES: National Institute of Environmental studies reference materials.

*Mean, \pm standard deviation ($n = 5$).

Table 3. Determination of thallium in water samples. Conditions and instrumental setting were same as Table 1.

Sample	Thallium added (μg)	Thallium found ^a (μg)	Recovery (%)
River water (Shahdad)	0.0	N.D. ^b	–
River water (Shahdad)	5.0	4.93 ± 0.05	98.6
River water (Shahdad)	20.0	19.71 ± 0.21	98.5
Tap water (Kerman)	0.0	N.D.	–
Tap water (Kerman)	5.0	4.98 ± 0.07	99.6
Tap water (Kerman)	10.0	9.95 ± 0.08	99.5
Tap water (Bardsir)	0.0	N.D.	–
Tap water (Bardsir)	5.0	4.89 ± 0.07	97.8
Tap water (Bardsir)	10.0	9.87 ± 0.11	98.7
Well water (Kerman)	0.0	B.L.R. ^c	–
Well water (Kerman)	5.0	5.04 ± 0.06	100.8
Well water (Kerman)	10.0	10.03 ± 0.16	100.3
Wastewater (Copper factory)	0.0	1.07 ± 0.08	–
Wastewater (Copper factory)	5.0	6.11 ± 0.12	100.8
Wastewater (Copper factory)	10.0	11.03 ± 0.21	99.6

Notes: ^aMean, \pm standard deviation ($n = 5$).

^bN.D.= Not detected.

^cB.L.R.= Below of linear range.

3.6 Analysis of water samples

In order to test the applicability and reliability of the proposed method, tap water, well water, river water and copper factory wastewater samples were analysed. For this purpose, 500.0 mL of each sample was filtered to remove suspended particles and was adjusted to pH 5.1. Then, 1 g of PAN loaded modified organo nanoclay was added to it with continuous stirring for 8 min, and then the solid mass was separated by filtration using filter paper No. 1041 (Whatman, UK). Finally, the separated solid was washed with distilled water. Adsorbed Tl ions were eluted with 5.0 mL of 5% ascorbic acid. The results are shown in Table 3. In all cases, the spiked recoveries confirmed the reliability of the

proposed method. The results showed that good recoveries were achieved for analysed samples.

4. Conclusion

The present study demonstrates the preparation and use of a sorbent based onto the PAN loaded modified nanoclay as a 'green' sorbent. Although in the literature it was reported that the PAN forms stable complex with Tl(III) [17], this work showed that the nature of PAN was changed while it adsorbed on nanoclay and PAN loaded modified nanoclay could complex with Tl(I) better than Tl(III). The presence of the nanoclay solid sorbent may also have an effect and lead to results different from that observed in a homogeneous reaction. The preparation of PAN loaded nanoclay is simple and at a low economic cost. The reagent remains in nanoclay, which allows the column to be used several times. Using this sorbent, a simple, precise, accurate and reliable method is developed for the preconcentration of trace thallium in different samples. The main advantages of this procedure are: (1) the preparation of the extractor system is simple and fast; (2) during thallium desorption, the PAN reagent remains in the sorbent; and (3) a good enrichment factor can be achieved.

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