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On-line preconcentration of ultra-trace thallium(I) in water samples with titanium dioxide nanoparticles and determination by graphite furnace atomic absorption spectrometry



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Abstract A new method has been developed for the determination of Tl(I) based on simultaneous sorption and preconcentration with a microcolumn packed with TiO₂ nanoparticle with a high specific surface area prepared by Sonochemical synthesis prior to its determination by graphite furnace atomic absorption spectrometry (GFAAS). The optimum experimental parameters for preconcentration of thallium, such as elution condition, pH, and sample volume and flow rate have been investigated. Tl(I) can be quantitatively retained by TiO₂ nanoparticles at pH 9.0, then eluted completely with 1.0 mol L⁻¹ HCl. The adsorption capacity of TiO₂ nanoparticles for Tl(I) was found to be 25 mg g⁻¹. Also detection limit, precision (RSD, *n* = 8) and enrichment factor for Tl(I) were 87 ng L⁻¹, 6.4% and 100, respectively. The method has been applied for the determination of trace amounts of Tl(I) in some environmental water samples with satisfactory results.

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1. Introduction

Nowadays heavy metals such as thallium have received considerable attention owing to their effects in the pollution of the environment. Many thallium(I) compounds are highly soluble in water and are readily absorbed through the skin. It has been identified to be an environmentally important element due to its toxic effects and because it is commonly found with lead, zinc, iron, tellurium and the alkalis. Tl is known to have side effects such as mutagenic, carcinogenic and teratogenic. Thallium(I) is highly toxic to the biosphere even more than Hg, Cd, Pb and

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Cu as well (Leonard and Gerber, 1997; Nriagu, 1998). Thallium is used as a catalyst, in making alloys, optical lenses, low temperature thermometers, dyes, pigment in scintillation counters and is used as medicines, rodenticides and insecticides as well (Lan and Lin, 2005). In human beings, poisoning from toxicological exposure to thallium occur in case of homicide, suicide and inadvertence (Günther and Kastenholz, 2005).

Owing to the toxicity of this metal and low concentration of thallium in aqueous environment (Das et al., 2007), an analytical technique which is presenting high sensitivity and low detection limit is required. Regarding to their high selectivity and sensitivity, atomic absorption spectrometry and particularly graphite furnace atomic absorption spectrometry (GFAAS) methods are extensively used for determination of thallium in various samples (Manning and Slavin, 1988). However, direct determination of thallium by GFAAS includes many difficulties due to spectral and non-spectral interferences in environmental matrices (Schmidt and Dietl, 1983; Shan et al., 1984). Other alternative is a GFAAS determination of thallium followed by separation and preconcentration (Cvetkovic et al., 2002; Bundalevska et al., 2005).

Numerous analytical methods have been proposed for separation and preconcentration of thallium, mainly based on liquid-liquid extraction (Asami et al., 1996), single drop liquid-phase microextraction (SDME) (Chamsaz et al., 2009), solid-phase extraction (SPE) (Lin and Nriagu, 1999; Mobarakeh and Mahani, 2005; Dadfarnia et al., 2007), coprecipitation (Stafilov and Čundeва, 1998) and ion-exchange (Jain et al., 1980).

Of all above methods, solid-phase extraction has attracted great attention for the preconcentration of traces of heavy metal ions owing to its simple operation, rapid phase separation, no emulsification, higher preconcentration factor and easy automation and combination with different detection techniques (Pyrzyska, 1998; de Godoi Pereira and Arruda, 2003). The selection of solid-phase extractant is the decisive factor that affects analytical sensitivity and selectivity. Various adsorbents such as silica C-18 (Urbánková and Sommer, 2008), Chromosorb 105 resin (Karatepe et al., 2011), Amberlite XAD resins (KOSHIMA, 1986), polyethylene (do Nascimento and Schwedt, 1997), activated carbon (Koshima and Onishi, 1985), microcrystalline naphthalene (Rezaei et al., 2007) and carbon nanotubes (Pacheco et al., 2009) have been investigated for preconcentration of thallium using SPE based on adsorption.

The nanometer material is usually a new functional material (Liang et al., 2000), which has attracted much attention due to its special properties (Watzke and Fendler, 1987). Most of the atoms on the surface of the nanoparticles are unsaturated that easily bind with other atoms. Nanoparticles have attracted much attention due to their special properties and high capacity of sorption. Moreover, the procedure is not only simple, but also the sorption process is rapid. So there is a growing interest in the application of nanoparticles as sorbents (Maria Claesson and Philipse, 2007). Recently it has been reported that titanium dioxide nanoparticles have been successfully used for separation and preconcentration of trace metal ions (Yang et al., 2004; Liang et al., 2007).

Thus, this paper aims to focus on the application of TiO₂ nanoparticles which are synthesized with a new method under ultrasonic irradiation at low intensity and to evaluate the adsorption properties of this nanomaterial for preconcentration

of Tl(I) using column method and coupled with GFAAS for the determination of the metal in water samples. Statistical properties of the method developed are presented.

2. Experimental

2.1. Apparatus

All measurements were carried out using a Perkin Elmer AAnalyst 800 graphite furnace atomic absorption spectrometer (Perkin Elmer Instruments, Shelton, CT, USA). The pH values were controlled with a Mettler Toledo 320-S pH meter (Mettler Toledo Instruments Co. Ltd., Shanghai, China) supplied with a combined electrode. Four-channel minipuls3 peristaltic pump (Gilson, Inc., USA) was used in the preconcentration process. A self-made PTFE microcolumn (40 mm × 3.0 mm i.d.), packed with nanometer size TiO₂, was used in all experiments. A minimum length of PVC tubing with an i.d. of 1.0 mm was used for all the connections.

2.2. Reagents and solutions

A stock solution (1000 mg L⁻¹) was prepared by dissolving solid Thallium nitrite(I) in aqueous solution. Thallium nitrate(I) (microscopy grade) was purchased from (Acros Organics, Geel, Belgium) and was used without any further purification. Working standard solutions were obtained by appropriate dilution of the stock standard solutions. Buffer solution at pH 9 (Merck, Darmstadt Germany) was used for conditioning the column in the preconcentration processes. Titanium tetra-isopropoxide (TTIP) (Merck, Darmstadt, Germany), ethanol (analytical grade) and glacial acetic acid 100% (Merck, Darmstadt, Germany) were used without any further purification. Glass beads with 40–60 mesh, was purchased from Glass beads Company (Glass beads Co., Tehran, Iran).

2.3. Preparation of TiO₂ nanoparticles

The titanium nanoparticles with diameter nearly 6 nm were prepared based on the method which is reported recently by Ghows and Entezari (2010). Fifty milliliters of deionized water and 0.2 mL acetic acid as a dispersant were mixed together in a sonication cell and sonicated. Then 2 mL titanium tetra-isopropoxide with 5 mL ethanol was injected drop-wise into an aqueous solution in 2 min. The mixture was sonicated continuously for 3 h at room temperature condition. The sonication was conducted without cooling so that the temperature was raised from 25 to 75 °C at the end of the reaction. The achieved precipitates were separated by centrifugation (20,000 rpm in 20 min) and washed three times with ethanol and deionized water. The product was dried at 40 °C for 24 h. Fig. 1a shows the TEM micrograph of TiO₂ nanoparticles. As shown, the diameter of the particles is estimated to be less than 10 nm. HRTEM image shows that the sample is a single crystal with a growing direction and a step of one atomic layer can be seen as well (Fig. 1b). The crystallinity of the product is also proven by selected area electron diffraction (SAED) as a crystallographic experimental method (insert in Fig. 1b).

2.4. Column preparation

A homogenous mixture of 20 mg of TiO₂ nanoparticles and 30 mg of glass beads with 40–60 mesh was introduced into a PTFE microcolumn (40 mm × 3.0 mm i.d.) plugged with a small portion of glass wool at both ends. Glass beads were used to facilitate the smooth flow of solution through the column and to probably increase the contact of solution with the surface of the nanoparticles. Before using, 1.0 mol L⁻¹ HCl solution and doubly distilled deionized water were passed through the column in order to clean and condition it. Then, the column was conditioned to the desired pH with 10 mL of 0.1 mol L⁻¹ NH₄Cl buffer solution.

2.5. General procedure

A portion of aqueous sample solution containing Tl(I) was prepared and the pH value was adjusted to desired value with 0.1 M HCl and NaOH. The solution was passed through the column by using a peristaltic pump adjusted to the desired flow rate. As the preconcentration was completed, the retained metal ions on the microcolumn were eluted with 1.0 mL of 1.0 M HCl solution. The analytes in the effluents were determined by GFAAS. The column could be used repeatedly after regeneration with 1.0 M HCl or HNO₃ solution followed by distilled water. Between the extractions, the microcolumn was dried by passing the air through it for 30 min.

3. Result and discussion

3.1. Effect of pH on adsorption

pH value plays an important role in the adsorption process due to the adsorption of different ions on TiO₂ surfaces. As said by Morterra (1988), the pH of solution affects the distribution of active sites on the surface of titanium dioxide nanoparticles. The surface charge is neutral at the isoelectric point (IEP), which is at pH 6.8 for TiO₂ nanoparticles (Zhang et al., 2009). In general, when the pH of the solution is higher than the isoelectric point of the adsorbent, the negative charge on the surface provides electrostatic attractions that are favorable for adsorbing cations such as thallium. In this experiment, the effect of the pH on the retention of thallium on the TiO₂ was studied in the range of 4–12 and operated according to the recommended procedure.

Fig. 2 shows the results of the effect of pH on the recoveries of thallium(I) ions by nanoparticles, which indicates that the adsorption percentage of the thallium sharply increases to the maximum as the pH increases to 9 and keep constant with the further increase of pH. Hence, in the following experiments the sample pH was adjusted to 9.

3.2. Elution of the adsorbed Tl(I) ions

It is found from Fig. 2 that the adsorption of thallium at pH < 4 could be negligible. Thus, various concentration of HCl were considered for the elution of retained Tl(I) from the microcolumn. Fig. 3 shows the effect of HCl concentration on the recovery of the adsorbed Tl(I). It can be seen that 1.0 M

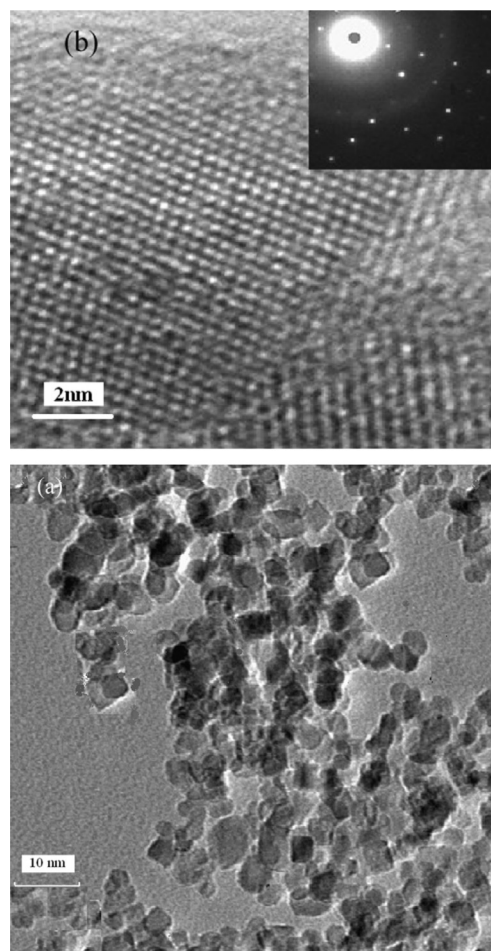


Figure 1 TEM (a), HRTEM and SAED (b) images.

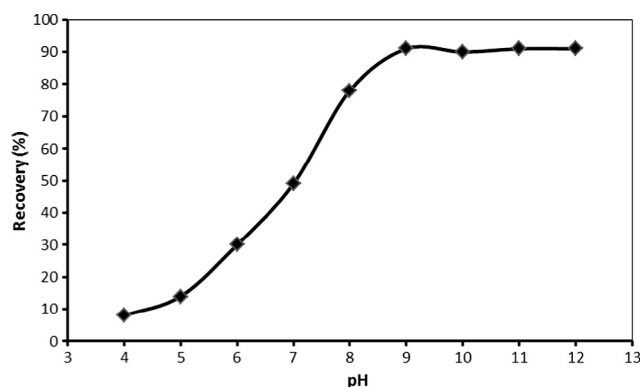


Figure 2 Effect of pH on the adsorption of Tl(I) on TiO₂ nanoparticles; Tl(I): 1.5 µg L⁻¹; sample volume: 50 mL.

HCl is enough to recover the Tl(I) quantitatively. Therefore, we applied 1.0 M HCl to recover the Tl(I) from microcolumn in this research. Then the effect of elution volume on the recovery of Tl(I) by keeping the HCl concentration equal to 1.0 M was studied. It was found that quantitative recoveries (>95%) could be achieved by 1.0 mL of 1.0 M HCl as the eluent.

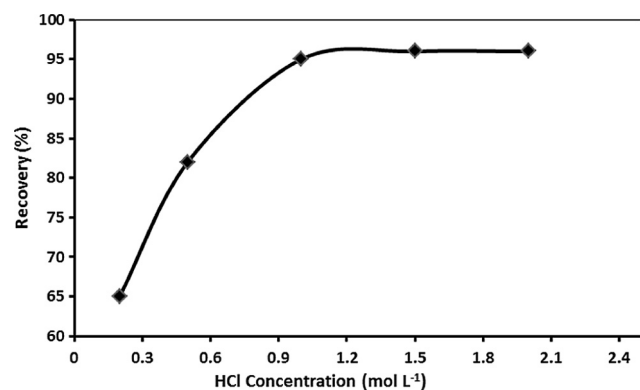


Figure 3 Effect of HCl concentration in the eluent on the recovery of Tl(I); Tl(I): $1.5 \mu\text{g L}^{-1}$; sample volume: 50 mL; pH: 9.0.

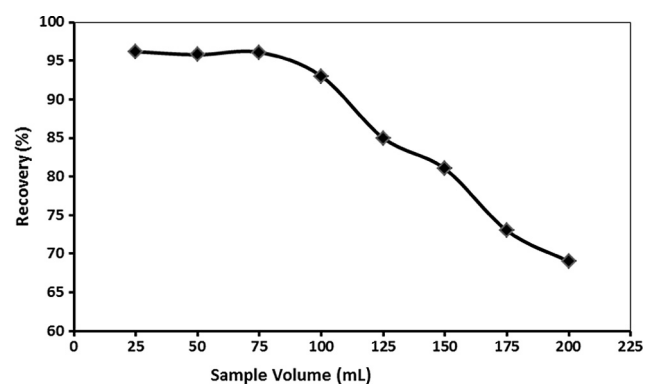


Figure 4 Effect of sample volume on the adsorption of Tl(I) on TiO_2 nanoparticles; Tl(I): $1.5 \mu\text{g L}^{-1}$; pH: 9.0.

3.3. Effect of flow rate of sample solution

The flow rate of sample solution affects the retention of Tl(I) on the nanoparticle as an adsorbent and it controls the time of analysis. Thus the influence of flow rate of sample solution on retention of Tl(I) ions in a range of $0.5\text{--}2.5 \text{ mL min}^{-1}$ under the optimum conditions (pH, eluent, etc.) was studied via passing 50 mL of sample solution through the microcolumn by a peristaltic pump. We observed that quantitative recovery ($>95\%$) of Tl (I) was obtained up to a flow rate of 1.5 mL min^{-1} and the recovery decreased when the flow rate was greater than 1.5 mL min^{-1} due to a decrease in the adsorption kinetics of reaction at higher flow rate. Thus, a flow rate of 1.5 mL min^{-1} was employed for subsequent investigations.

3.4. Effect of sample volume

In order to investigate the possibility of achieving high levels of enrichment factor, we examined the effect of sample volume on recovery of Tl(I). To achieve to this goal, a series of sample solution over the range of 25–200 mL containing a fixed quantity of Tl(I) were processed based on the recommended procedure. The results were exhibited in Fig. 4.

According to this figure, as shown, quantitative recovery ($>95\%$) of thallium was obtained for sample volumes of

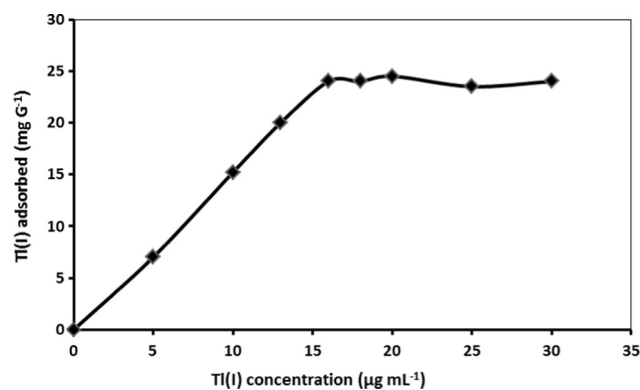


Figure 5 Adsorption isotherm of Tl(I) on TiO_2 nanoparticles; pH: 9.0; sample volume 30 mL.

Table 1 Tolerance limits for coexisting ions for adsorption of Tl(I) $1.5 \mu\text{g L}^{-1}$.

Coexisting ions	Tolerance limit of ions ($W_{\text{ion}}/W_{\text{Tl(I)}}$)
Na^+ , K^+	1000
Ca^{2+} , Mg^{2+}	500
Fe^{3+} , Al^{3+}	200
Sb^{3+} , Pb^{2+}	50
Zn^{2+} , Ni^{2+} , Cu^{2+} , Cd^{2+}	200
PO_4^{3-} , SO_4^{2-} , Cl^- , NO_3^-	500

Table 2 Analytical performance of the proposed method toward the Tl(I) ion.

R^2	Limits of detection (ng L^{-1})	Linear range ($\mu\text{g L}^{-1}$)	RSD (%) ($n: 8$)
0.9986	87.0	0.6–2.5	6.4

$\leq 100 \text{ mL}$ for Tl(I) ions. Thus, the adsorbed Tl(I) can be eluted with $1.0 \text{ mL } 1.0 \text{ mol L}^{-1} \text{ HCl}$, so the enrichment factor of 100 was achieved by this method.

3.5. Adsorption capacity

Adsorption capacity is one of the important parameters in assessment of the adsorption capacity of different adsorbents, since it suggests how much adsorbent is required to quantitatively concentrate the analyte from a solution. The capacity study method which is used was the one adapted from that recommended by Maqueira et al. (1994). To determine the adsorption capacity, 30 mL aliquots of sample solutions containing the different Tl(I) concentrations (in the range of $0\text{--}30 \mu\text{g mL}^{-1}$) were adjusted to the appropriate pH with $0.1 \text{ mol L}^{-1} \text{ HCl}$ or NaOH . Then 20 mg of TiO_2 nanoparticles was packed in microcolumn and the preconcentration procedure described above was applied. The amount of Tl(I) adsorbed at each concentration level was determined. The profile of the adsorption isotherm for thallium was gained by plotting the concentration ($\mu\text{g mL}^{-1}$) of Tl(I) solution versus the milligrams of Tl(I) adsorbed per gram TiO_2 nanoparticles, and shown in Fig. 5. The result from the adsorption isotherm

Table 3 Comparison of the proposed method in this work with some established methods using solid-phase extraction for thallium.

Adsorbent	Detection method	Species	Enrichment factor	Detection limit ($\mu\text{g L}^{-1}$)	Reference
2,6-Bis(<i>N</i> -phenyl carbamoyl)pyridine naphthalene Chromosorb 105 resin	UV-vis	Tl(III)	100	0.25	Rezaei et al., 2007
	ETAAS	Total Tl	150	0.050	Karatepe et al. (2011)
Thallium(III) ion imprinted polymer	GFAAS	Tl(III)	10	0.02	Arbab-Zavar et al. (2011)
Multiwalled carbon nanotubes Immobilized oxine	GFAAS	Tl(III)	20	0.009	Gil et al. (2009)
	FAAS	Tl (total)	100	2.5	Dadfarnia et al. (2007)
Thiol cotton fiber (TCF)	GFAAS	Tl(I)	–	0.003	Yu et al. (2001)
Sawdust	FAAS	Tl(I)	160	12.5	Memon et al. (2008)
Modified silica SGX C18	ICP-AES	Tl(III)	100	0.72	Urbánková and Sommer (2008)
Titanium dioxide nanoparticles	GFAAS	Tl(I)	100	0.087	This work

shows that the adsorption capacity of TiO_2 for Tl(I) was found to be 25 mg g^{-1} .

3.6. Column reuse

The stability and potential regeneration of the microcolumn packed with TiO_2 nanoparticle were investigated. The column can be reused after regenerated with 10 mL 1.0 mol L^{-1} HCl followed by 20 mL deionized water. After repeating this process 15 times, the recovery of Tl(I) was still above 95%. Thus the microcolumn packed with TiO_2 nanoparticles can be reused at least 15 times.

3.7. Effects of coexisting ions

The effect of common coexisting ions on the thallium retention onto TiO_2 nanoparticles was evaluated using the developed method. The existence of coexistence ions would affect the preconcentration of thallium by competitive adsorption. In these experiments, various foreign cations and anions at various concentrations were added to $1.5 \mu\text{g L}^{-1}$ Tl(I) at pH 9 and enriched in microcolumn according to the recommended procedure. The tolerance limits of the coexisting ions, defined as the largest amount making the recovery of Tl(I) less than 95%, were given in Table 1. It can be seen that the presence of coexisting ions at a much higher level has no obvious effect on the adsorption of Tl(I) ion under the selected conditions.

3.8. Analytical performance of the method

The calibration curve for Tl(I), based on optimal conditions, was linear with a correlation coefficient of 0.9986 in the range of $0.6\text{--}2.5 \mu\text{g L}^{-1}$. Also in accordance with the definition of IUPAC (Long and Winefordner, 1983), the detection limit of this method, evaluated as the concentration corresponding to three times the standard deviation of 11 runs measurements of blank solution using the preconcentration method, was found to be 87 ng L^{-1} for Tl(I). The results (Table 2) show that the precision of this method (RSD), examined by eight replicate measurements of $1.5 \mu\text{g L}^{-1}$ Tl(I) in 100 mL of model

Table 4 Determination of Tl(I) ($\mu\text{g L}^{-1}$) in blank and spiked real environmental samples.

Samples	Added	Found	Recovery (%)
Tap water	0	0.2 ± 0.2	
	1	1.1 ± 0.1	90.0
	2	2.1 ± 0.09	95.0
Mines lake water	0	0.3 ± 0.2	
	1	1.2 ± 0.2	95.0
	2	2.2 ± 0.2	96.5

solutions, was about 6.4% and indicating that the method has good precision for the analysis of trace Tl(I) ions in solution samples.

Table 3 compares the characteristic data of the present method with some other methods reported in literatures. As can be seen, the enrichment factor and detection limits obtained by the present method are comparable to those reported method, and it can be used efficiently for sample containing thallium.

3.9. Application of the method on real waters

In order to establish the performance of preconcentration method in determination of Tl(I) in real samples, two environmental water samples (tap water and Mines lake water) were collected from the region of Serdang city in Malaysia and used for the mentioned analysis. In these experiments, the samples were spiked with 1.0 and $2.0 \mu\text{g L}^{-1}$ Tl(I) and subjected to the preconcentration procedure. The results (Table 4) indicate that proposed method could be used to determine thallium in real water samples.

The method has been applied for the determination of Tl(I) in the standard reference material (JR-1) for its thallium content as well. The rock sample (0.5 g) was dissolved in 10 mL of mixture of HF (25 mL), HNO_3 (2 mL) and H_2SO_4 (8 mL) in a teflon beaker, and heated until 2 mL of solution was remained. Eight milliliters of concentrated HNO_3 was added to this solution and after heat treatment distilled water was added to give

a clear solution and was finally made to 100 mL by further addition of distilled water. This solution was analyzed for its Tl content according to the proposed procedure and was determined to be $1.55 \pm 0.18 \mu\text{g g}^{-1}$ which is in good agreement with its certified value ($1.56 \mu\text{g g}^{-1}$) with a recovery of 99.3%.

4. Conclusions

TiO₂ nanoparticles have been successfully synthesized by Sonochemical method and used as the microcolumn packing material for preconcentration of Tl(I) prior to its determination by graphite furnace atomic absorption spectrometry. The results obtained indicate that TiO₂ nanoparticles are effective SPE sorbents for the adsorption of Tl(I) from aqueous solutions. The precision and accuracy of proposed method were satisfactory and percentage of Tl(I) removal from solution is close to 100% at pH 9. Also The TiO₂ nanoparticles prepared by this method show a remarkable adsorption capacity of 25 mg g^{-1} for Tl(I) ions. The method can be successfully applied to the separation, preconcentration and determination of Tl(I) in environmental samples.

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