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Solid Phase Extraction and Flame Atomic Absorption Spectrometry for the Determination of Trace Thallium

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Based on the separation and preconcentration of thallium(III) by solid phase extraction with N-(3,5-dimethylphenyl)-N'-(4-aminobenzenesulfonate)thiourea (DMMPT) loaded on graphitized carbon black as a sorbent, a new method for the determination of thallium was developed. The preconcentrated Tl(III) was eluted from the cartridge with 1.0 mL of 0.5 mol L^{-1} HNO_3 as eluant and then the thallium(III) contents was measured by flame atomic absorption spectrometry. Under the optimum conditions, a preconcentration factor of 1000 was achieved. The detection limit of the method reaches 0.05 μg L^{-1}. The method was successfully applied for the determination of thallium in biological sample and water. The relative standard deviations were below 3.4 % with recoveries of 88-106 % and the determination results were agreed with that of reference method.

Key Words: Thallium, N-(3,5-dimethylphenyl)-N'-(4-aminobenzenesulfonate)thiourea, Graphitized carbon black, Solid phase extraction, Flame atomic absorption spectrometry.

INTRODUCTION

Thallium is a non-essential toxic element with no known beneficial biological role, which has various industrial applications[1,2] such as semiconductors, nuclear medicine, catalysts, dyes and pigments; thereby increasing the risk of occupational poisoning and environmental pollution. It is known that Tl is more toxic than Hg, Pb, Cu and Cd[3,4]. Therefore, the development of new methods for selective determination of Tl in sub micro levels is received more and more attentions.

Flame atomic absorption (FAAS) are the most widely methods used for trace thallium determination[5-7]. However, because of the limited sensitivity of the FAAS, complex matrices and the low thallium concentration levels in natural samples, the thallium determination frequently requires a previous separation and pre-concentration steps. The most widely used preconcentration methods are coprecipitation, ion exchange, solvent extraction, flotation and solid phase extraction (SPE)[5,6,8-11].

Solid phase extraction is an attractive separation-preconcentratio technique for thallium ions and various solid phase extraction materials have been successfully

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used for the preconcentration and separation of thallium at trace levels[6,12-18]. At this point, graphitized carbon black has been proposed as a novel solid phase extraction sorbents because it possess excellent adsorption ability[20-22]. However, the application of graphitized carbon black as sorbent for Tl determination had not been reported yet. N-(3,5-Dimethylphenyl)-N'-(4-aminobenzene-sulfonate)thiourea (DMMPT) is a spectrophotometric reagent synthesized in our laboratory. It can react with thallium at room temperature rapidly[23] and can also be adsorbed on graphitized carbon black surfaces which is completely stable. This means that the graphitized carbon black cartridge can be used several times without decreasing the enrichment factor. Based on this, a method for the determination of thallium by FAAS using graphitized carbon black as sorbent and DMMPT as complexing agent was developed.

EXPERIMENTAL

Carbopack™ B graphitized carbon black (60-80 mesh) was obtained from Sigma-Aldrich Corporation (USA). All solutions were prepared with double distilled water. Otherwise stated, analytical-grade acids and other chemicals were obtained from Merck (Darmstadt, Germany).

The DMMPT (Fig. 1) was synthesized according to previous literature[22] and DMMPT solution (1.0 %, m/v) was prepared by dissolving 1.0 g of the reagent in ethanol.

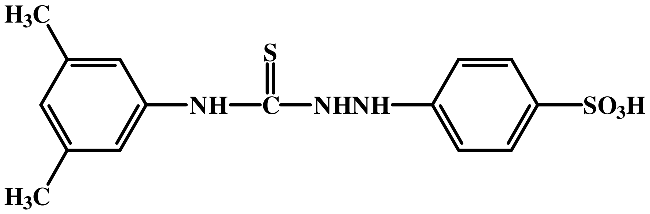

Fig. 1. Structure of DMMPT

Buffer solutions (pH 1.0-9.0) were made of mixture of acetic acid, boric acid and phosphoric acid plus sodium hydroxide in water.

Preparation of modified graphitized carbon black cartridge: In a 50 mL beaker, 10.0 g of graphitized carbon black was added to 10 mL ethanolic solution of DMMPT (1.0 %) and mixed well. The ethanol was evaporated and the modified graphitized carbon black was obtained. A teflon cartridge (0.8 cm length and 0.5 mm in diameter, Fig. 2.) was packed with 0.25 g of the modified graphitized carbon black.

A Perkin-Elmer Model A Analyst 600 atomic absorption spectrometer equipped with a Model AS-800 autosampler (Norwalk, CT) and furnished with a thallium hollow-cathode lamp was used. The instrument was adjusted according to the standard conditions: Lamp current 3.0 mA, wavelength 377.6 nm, air-acetylene flame (air flow rate 7.0 L min^{-1}, acetylene flow rate 1.6 L min^{-1}), spectral band width 0.2 nm.

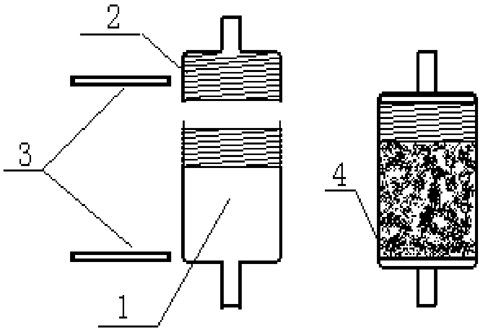

Fig. 2. SPE cartridge (1) tube for fill in the sorbent, (2) screw cap for sealing the tube), (3) sieve plate, (4) modified graphitized carbon black

The pH of aqueous solutions was checked using a Beckman F-200 pH meter with a glass electrode.

Procedure: A 50-1000 mL of Tl(III) solution, buffered at pH 3.5 (acetic acid-sodium acetate buffer, 0.01 mol L^{-1}), was passed through the cartridge at a flow rate of 10.0 mL min^{-1}. After finishing the sample solution, a volume of 1.0 mL of 0.5 mol L^{-1} HNO_3 was passed through the cartridge in the reverse direction at a flow rate of 1.0 mL min^{-1} to elute the Tl(III) ions. The eluant was afforded to FAAS determination.

For river water and tap water, the pH of the sample was adjusted to 3.5 and the solution was passed through the cartridge. Thallium ions retained on the cartridge were eluted with 1.0 mL of 0.5 mol L^{-1} HNO_3. The eluent was analyzed by the flame atomic absorption spectrometry.

For human hair and nail sample, the samples were rinsed with acetone, chloroform and doubly distilled water and was dried at 60 ºC. An exact amount (1.0 g) of dried samples was placed into the 50 mL Teflon high-pressure microwave acid-digestion bomb. To which, 1.0 mL of concentrated nitric acid and 10.0 mL of 30 % hydrogen peroxide was added. The bombs were sealed tightly and then positioned in the carousel of the microwave oven. The system was operated at full power for 10 min. The digest was evaporated to near dryness. The residue was dissolved with 15 mL of 5 % HNO_3 and the pH of the sample was adjusted to 3.5 with 5 % NaOH. Afterwards, the above preconcentration procedure was applied to the final solutions and the blank solution.

RESULTS AND DISCUSSION

Optimization of variables: First of all, to obtain the best quantitative recoveries of Tl(III) ions, many parameters such as pH of sample solution, sample volume, the concentration of washing solution, sample flow-rate through the cartridge, capacity of the modified graphitized carbon black and the effect of matrix on the preconcentration step should be studied.

In the optimization steps, 0.25 g of graphitized carbon black was used. The influence of pH of sample solution on the preconcentration step of Tl(III) was also studied. For this purpose, 400 mL of 0.05 μg mL^{-1} Tl(III) at different pH values (1.0-9.0) was passed through the modified solid phase. Then the Tl(III) concentration in eluent solution was checked using FAAS. The results (Fig. 3.) showed that the suitable pH for adsorption of Tl(III) on the modified graphitized carbon black is around 2.5-5.5. Therefore, a buffer solution (acetic acid-sodium acetate, 0.01 mol L^{-1}) at pH 3.5 was used for the preconcentration step.

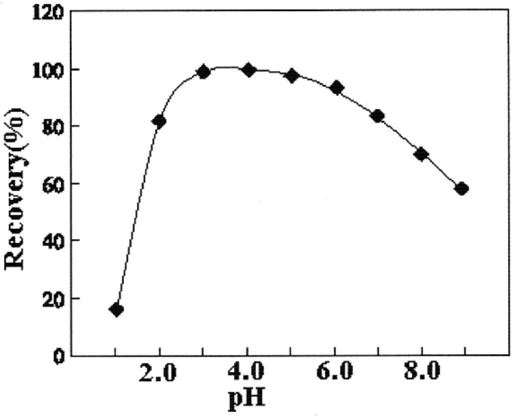

Fig. 3. Influence of pH of the sample solution on adsorption of Tl(III) on the modified graphitized carbon black. Conditions: Initial Tl(III) value, 200 mL of 0.05 μg mL^{-1}; washing solution, 1.0 mL of 0.50 mol L^{-1} HNO_3

For desorption of Tl(III) from the solid phase, different HNO_3 concentrations (1.0 mL) in the interval range of 0.5 to 2.0 mol L^{-1} with flow rate of 1.0 mL min^{-1} and with sample flow rate of 10 mL min^{-1} were tested for the quantitative elution of the adsorbed Tl(III) ions from the cartridge. The results showed that 0.5 mol L^{-1} HNO_3 was suitable to remove (100 ± 2.5) % of Tl(III) from the solid sorbent. In order to optimize the volume of 0.5 mol L^{-1} HNO_3 solution, 100 mL of 0.2 μg mL^{-1} Tl(III) was passed through a series of the modified graphitized carbon black under the optimum conditions. Then the solid phases were washed with different volumes of 0.50 mol L^{-1} HNO_3 (0.5-6.0 mL). The results showed that it is easier to elute the retained Tl(III) in the reverse direction in comparison to the forward direction (only 1.0 mL of HNO_3 solution was needed when eluted in reverse direction. However, 3.0 mL of HNO_3 solution was needed when eluted in forward direction). Thus, it is also recommended to invert the cartridge before elution.

The influence of the sample flow rate on preconcentration efficiency of Tl(III) ions through the cartridge was also investigated. For this purpose, a volume of 50 mL of 0.2 μg mL^{-1} Tl(III) solution at pH 3.5 was passed through a series of cartridge at different flow rates. Then the adsorbed Tl(III) was washed with 1.0 mL of 0.5 mol L^{-1} HNO_3 solution and the Tl(III) content was measured using FAAS. The results showed that using a sample flow rate greater than 12 mL min^{-1} can caused a decrease of the Tl(III) ions recoveries. Therefore, a sample flow rate of 10.0 mL min^{-1} was used for further studies.

The effect of flow rate of HNO_3 (0.5 mol L^{-1}) on desorption efficiency of Tl(III) ions from the cartridge was also checked in the range of 1.0-5.0 mL min^{-1}. The results showed that the recovery of thallium was maximized when using elution rates up to 1.0-2.5 mL min^{-1}. Therefore, 2.0 mL min^{-1} was selected.

The capacity of the modified graphitized carbon black for adsorption of Tl(III) was checked by passing 150 mL of Tl(III) solution containing 0.05-10 μg mL^{-1} Tl(III) through the cartridge (containing 0.25 g modified graphitized carbon black). The thallium was stripped off the modified graphitized carbon black with 1.0 mL 0.5 mol L^{-1} HNO_3 and measured by FAAS. Under the condition of thallium recovery ≥ 95 %, the adsorption capacity was calculated to be 0.76 mg g^{-1}. The cartridge has adequate capacity to enrich the thallium in real sample.

Reusability of the modified graphitized carbon black was checked using the same solid phase for sorption-desorption of Tl(III) ions for 50 times the reusability was tested. The maximum change in the performance (sorption capacity) of the solid phase after the repeated use was less than 2 %, indicating that its repeated use is feasible as leaching of the dye from the graphitized carbon black matrix is insignificant. No change in the sorption capacity of the modified graphitized carbon black was noticed after storing it for 2.0 months.

Calibration graphs and detection limits: Under the FAAS analysis conditions, regression equations of Tl(III) was established based on the standard samples injected and their absorption signals. The results showed that the linearity range for thallium was obeyed in the range of 0.1-10 μg mL^{-1} and the linear regression equation obtained was: $A = 0.00284 + 0.0387\ C$ (μg mL^{-1}), $r = 0.9996$.

The results showed that the limit of quantitative preconcentration was 0.2 μg L^{-1} Tl(III) with a preconcentration factor of 1000 (1000 mL of sample solution was passed the cartridge). Recoveries from further diluted solutions or larger sample volume were not quantitative (the recovery of thallium < 95 %). The limit of detection values based on three times the standard deviations of the blank was equal to 0.05 μg L^{-1} Tl(III).

Interference study: The influence of matrix ions in water samples on the separation and recovery of Tl(III) ions was also investigated by passing different amounts of potential interfering ions plus 50.0 ng mL^{-1} Tl(III). The results showed that 10000-fold of alkaline and alkaline-earth ions, chloride, nitrate, hydrogen carbonate, carbonate and sulfate, 500-fold Zn(II), Fe(II), Ni(II), Pd(II), V(III), Mn(II), Cu(II), Hg(II), Al(III), Mo(VI), Co(II), Cr(III), Ag(I), Pb(II), did not interfere. The results confirm that the modified solid phase is highly selective for Tl(III) and interferences did not occur.

Application to real samples: The method was applied to the determination of thallium in biological samples and water. The results (deducted the reagents blank) were given in Table-1. A standard method using ICP-MS had also been used as reference method and the result were also shown in Table-1.

TABLE-1
RESULTS OF THE WATER AND BIOLOGICAL SAMPLES

Samples	ICP-MS method	This method	RSD % (n=7)	Recovery (%) (n=5)
Tap water	0.260 (μg/L)	0.240 (μg/L)	3.2	88-102
River water	1.220 (μg/L)	1.340 (μg/L)	3.4	91-106
Human hair	0.384 (μg/g)	0.395 (μg/g)	3.0	90-98
Nail	0.675 (μg/g)	0.668 (μg/g)	3.2	88-97

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