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Multi-walled carbon nanotube modified with 1-buthyl 3-methyl imidazolium hexaflouro phosphate supported on sawdust as a selective adsorbent for solid phase extraction of Bi(III)

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ABSTRACT

Multi-walled carbon nanotube (MWCNT) was dispersed and loaded with 1-buthyl 3-methyl imidazolium hexaflouro phosphate ([BMIM]PF_6), supported on sawdust and used as a new adsorbent for preconcentration of trace amount of bismuth. In this method, Bi(III) ions are retained by the adsorbent in a column after formation of negative complex with iodide. BiI_4^- complexes are retained on MWCNT-[BMIM]PF_6 through the electrostatic interactions with positive charge of imidazolium ion. The adsorbed complex is eluted from the column with a solution of nitric acid and determined by flame atomic absorption spectrometry (FAAS). The effect of various parameters, such as pH, sample volume, concentration and volume of nitric acid as eluent, iodide concentration in sample solution, and interfering ions was investigated in order to achieve highest sensitivity. The calibration graph was linear in the range of 4–300 ng mL^{-1} for Bi(III) in the initial solution. The limit of detection based on $3S_b$ was 2.3 ng mL^{-1} for Bi(III). The relative standard deviation for ten replicate measurements of 20 and 80 ng mL^{-1} was 2.3 and 0.98%, respectively. The method was applied to the determination of Bi(III) ions in river water, tap water and drug samples.

1. Introduction

Bismuth and its compounds are used in semiconductors, cosmetic preparations, alloys, and metallurgical additives as well as in the preparation and recycling of uranium nuclear fuels. Since the use of bismuth and its compounds in different areas of life has increased, toxicity of this element started to be considered for humans, animals and plants [1]. Bismuth is present in seawater at a very low concentration of about 10^{-10} mol L^{-1} (20 ng dm^{-3}). It is also used in medicine due to its anti-acid action and mildly astringent action in gastrointestinal disorders [2]. Although the absorption of Bi(III) in the human organism is generally low, several cases of nephrotoxic, neurotoxic, and kidney damage symptoms attributable to the use of Bi(III) containing pharmaceutical formulations have been reported. Therefore determination of bismuth is an important task in environmental chemistry, cosmetic industry, semiconductors, alloys, medicine, metallurgical additives and fabrication of catalysts.

Various analytical techniques have been reported for the determination of Bi(III) in different samples such as alloy, water, rock, and biological samples. These include spectrophotometry [3] Flame atomic absorption spectrometry (FAAS) [4] electrothermal vaporization atomic fluorescence spectrometry [5], hydride generation atomic absorption [6,7], adsorptive anodic stripping voltammetry [8], electrothermal vaporization ICP mass spectrometry (ETV-ICP-MS) [9] and hydride generation inductively coupled plasma atomic emission spectrometry (HG-ICP-AES) [10]. The techniques mentioned above such as ICP-OES, ET-AAS and ICP-MS are expensive and are not available in many laboratories because of their high costs. Compared to these techniques, FAAS has the advantages of low cost and simplicity, but direct determination of bismuth is seldom carried out due to the relatively poor sensitivity [11]. Therefore a preconcentration procedure is often required to improve the detectability of FAAS. Among preconcetration methods, solid phase extraction has gained popularity in recent years [12–14]. The selection of appropriate adsorbent is a critical factor in the preconcentration of metal ions in order to obtain full recovery and high adsorption capacity. In recent years, application of nano-structure materials, especially carbon nanotubes (CNTs) have been of great importance due to their high surface area, good chemical stability, high electrical conductivity and unique tubular structure. MWCNTs have been used for the preconcentration of trace amounts of organic materials and the extraction of metal ions from environmental samples [15–19]. As any carbon-based material, there is a possibility of altering the surface properties of the carbon

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nanotubes. CNTs can be functionalized in different ways and used as adsorbents [20].

Room-temperature ionic liquids are organic salts with properties being easily adjusted by changing one of the ions [21–23]. They are green solvents with unique physicochemical characters such as thermal stability, relatively low viscosity, and high ionic conductivity [24–26]. Room temperature ionic liquids have been used as solvents for inorganic and organic materials as well as polymers [27–29]. Ionic liquids and various surfactants have been extensively used for dispersion of carbon nanotube [30–32]. But dispersion using surfactants can be easily removed by washing and therefore dispersion of nanotubes in surfactants may not be a good choice for preconcentretion applications. However ionic liquids can disperse a higher concentration of CNTs than SDS or DNA assisted methods and the treatment process for dispersing CNTs in ionic liquids is very simple. The interaction between CNTs and ionic liquids is also a weak van der Waals force, just like that between CNTs and SDS molecules or DNA [33].

In this paper, a new solid-phase extraction method for the determination of Bi(III) is described. The method is based on the adsorption of negative complexes of bismuth with iodide on multi-walled carbon nanotube (MWCNT) dispersed and loaded with 1-butyl-3-methyl imidazolium hexafluorophosphate ([BMIM]PF_6), room temperature ionic liquid and supported on sawdust in a column. The bismuth ions are then eluted with nitric acid and determined by FAAS.

2. Experimental

2.1. Instrumentation

A GBC flame atomic absorption spectrometer model Avanta (Sidney, Australia) was used for the determination of bismuth. It was equipped with bismuth hallow cathode lamp and air–acetylene burner. The instrumental parameters were as follows: wavelength 223.1 nm, lamp currents 10 mA and band pass 1.0 nm.

All pH measurements were made using a Metrohm digital pH meter model 632 (Herisau, Switzerland) with a combined glass electrode.

2.2. Chemical and reagents

Analytical reagent-grade chemicals were used. Stock solution of bismuth (100 mg L^{-1}) was prepared by dissolving 0.0232 g of bismuth nitrate [$Bi(NO)_3 \cdot 5H_2O$] (Merck, Darmstadt, Germany) in 10 mL of 1.0 mol L^{-1} of nitric acid and diluting to 100 mL with distilled water. 1.0 mol L^{-1} solution of potassium iodide was prepared by dissolving 16.62 g of potassium iodide (Merck) and diluting to 100 mL in a volumetric flask. 3.0 mol L^{-1} solution of nitric acid was prepared by diluting 20.9 mL of HNO_3 (Merck, 65%, d=1.4 g mL^{-1}) to 100 mL in a volumetric flask. An acetate buffer solution was prepared by adding 0.2 mol L^{-1} NaOH to 0.2 mol L^{-1} acetic acid and adjusting the pH to 4.60 using a pH meter.

MWCNT was purchased from Neutrino (Tehran, Iran) and [BMIM]PF_6 was purchased from Kimia Exir (Tehran, Iran) and used as received.

Pine tree sawdust was collected from a local sawmill. It was washed with water to remove dust, dried at 45 °C in an electrical oven for 30 min and passed through a mesh 20 sieve.

2.3. Adsorbent preparation

0.1 g of MWNTs was dispersed in 1 g of [BMIM]PF_6 by grinding in a mortar for about 1 h. The positively charged imidazolium ion would wrap (or adsorb) on the surface of MWNTs in the course of grinding, and a resultant MWCNT-[BMIM]PF_6 composite would be formed. The suspension was then mixed thoroughly with 5 g of pine sawdust until it would be black. This adsorbent was stored for further use.

2.4. General procedure

A glass tube (10 cm length and 1 cm i.d) with a very fine bore was used as a preconcentration column. It was filled with the 0.2 g adsorbent and slightly pressed in the column with a flat glass rod (column length was 2.0 cm). The ends of the column were fitted with cotton to retain the packing material. 500 mL of the solution containing 4–300 ng mL^{-1} of Bi(III), 3 mL of acetate buffer solution (pH=4.6) and 10 mL of 1 mol L^{-1} of potassium iodide solution was passed through the column at a flow rate of 20 mL min^{-1}. The metal complexes adsorbed on MWCNT-[BMIM]PF_6 supported on sawdust were eluted with 1.5 mL of 3 mol L^{-1} of nitric acid. The metal content of the eluent was determined by FAAS. A blank solution was also run under the same analytical conditions without adding any Bi(III). The recovery of Bi(III) adsorbed on the column was calculated from the amounts of Bi(III) in the starting sample and the amounts eluted from the column.

2.5. Sample preparation

For preparation of tablet samples, 0.01 g of bismuth subcitrate tablet was completely dissolved in 5 mL of concentrated HNO_3. The mixture was heated to dryness. Three consecutive additions of 10 mL distilled water were then made and each time the solution evaporated almost to dryness to eliminate the excess acid. The residue was dissolved in distilled water and filtered using a filter paper (Whatman No. 1). The filtrate solution was diluted to 100 mL with distilled water in a volumetric flask. An aliquot of this solution was analyzed for determination of bismuth using the procedure described above.

The water samples were collected, acidified and kept in a refrigerator and filtered before use. An aliquot of water samples were treated under the recommended procedure.

3. Results and discussion

Recently, it has been shown that CNTs can be easily dispersed in the imidazolium based room-temperature ionic liquids by mechanical milling, forming a thermally stable gel (bucky gel) [33]. Based on the above discussion, multi-walled carbon nanotube (MWCNT) was dispersed and loaded with 1-butyl-3-methyl imidazolium hexafluorophosphate ([BMIM]PF_6) room temperature ionic liquid and supported on sawdust. This composite was used as a new adsorbent for the determination of Bi(III).

Iodide ion forms complex with a number of metal ions including bismuth. At high concentration of iodide negative complexes with formulas BiI_4^- or BiI_6^{3-} are formed between Bi(III) and iodide ions [34]. Bismuth triiodie is a black precipitate which is dissolved in excess iodide solutions to yield these complexes. These negatively charged complexes are capable of forming ion pair with the positive sites of MWCNT-[BMIM]PF_6 supported on sawdust.

3.1. Effect of pH

The solution pH is an important parameter for achieving quantitative adsorption and recovery of trace elements on the adsorbent. In order to optimize the pH for the retention of Bi(III) on MWCNT-[BMIM]PF_6 adsorbent, the recovery of bismuth was