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ORIGINAL ARTICLE

Graphene for separation and preconcentration of trace amounts of cobalt in water samples prior to flame atomic absorption spectrometry

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Abstract A new sensitive and simple method was developed for the preconcentration of trace amounts of cobalt (Co) using 1-(2-pyridylazo)-2-naphthol (PAN) as chelating reagent prior to its determination by flame atomic absorption spectrometry. The proposed method is based on the utilization of a column packed with graphene as sorbent. Several effective parameters on the extraction and complex formation were selected and optimized. Under optimum conditions, the calibration graph was linear in the concentration range of 5.0–240.0 $\mu g\ L^{-1}$ with a detection limit of 0.36 $\mu g\ L^{-1}$. The relative standard deviation for ten replicate measurements of 20.0 and 100.0 $\mu g\ L^{-1}$ of Co were 3.45 and 3.18%, respectively. Comparative studies showed that graphene is superior to other adsorbents including C18 silica, graphitic carbon, and single- and multi-walled carbon nanotubes for the extraction of Co. The proposed method was successfully applied in the analysis of four real environmental water samples. Good spiked recoveries over the range of 95.8–102.6% were obtained.

1. Introduction

Cobalt is a naturally occurring element found in rocks, soil, water, plants, and animals. It is an essential micronutrient required for the growth of both plants and animals (Lemos et al., 2007). Cobalt can be beneficial for humans because it is part of vitamin B_{12} and since humans are unable to synthesize it, there is a need to ingest foods that contain it, such as fish, oysters, eggs, milk, and green vegetables (Underwood, 1977; Belitz and Grosch, 1987). The recommended dietary allowance (RDA) for vitamin B_{12} for adults is 2.4 $\mu g\ day^{-1}$, which contains 0.1 μg of cobalt. Intake of less than this amount can lead to deficiency and to diseases such as pernicious anemia (Agency for Toxic Substances and Disease Registry [ATSDR], 2001). On the other hand, large amounts of cobalt can produce toxicological effects including vasodilation, flushing and cardiomyopathy in humans and animals (Chen and Teo, 2001). Therefore, the development of accurate and efficient determination methods for monitoring the level of cobalt

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concentration in the environmental samples is necessary and indispensable.

Several modern instrumental methods including spectrometry, atomic absorption spectrometry (AAS), inductively coupled plasma atomic emission spectrometry (ICP-AES), and inductively coupled plasma mass spectrometry (ICP-MS), etc., have been used for determining traces of metal ions in various media (Dos Santos et al., 2005; Sreenivasa Rao et al., 2002; Dadfarnia and McLeod, 1994). However, due to low concentrations of metal ions in environmental samples and matrix interferences, the determination of metal ions in complex matrices is limited and requires preconcentration and/or separation of analytes to improve sensitivity and selectivity of analyses (Brown and Milton, 2005; Becker, 2005). Up to now, several methods have been designed for separation/preconcentration of cobalt from various matrices, including liquid–liquid extraction (LLE) (Gupta and Khopkar, 1995), solid-phase extraction (SPE) (Yamini et al., 2004), coprecipitation (Divrikli and Elçi, 2002) and cloud point extraction (CPE) (Safavi et al., 2004), etc.

Among these techniques, solid-phase extraction (SPE) is a popular technique for achieving separation and preconcentration of metal ions in environmental samples (Safavi et al., 2006; Tuzen et al., 2008) has been developed and widely used because of its simplicity, rapidity, minimal cost, low consumption of reagents and the ability to combine with different detection techniques whether in on-line or off-line mode (Fritz, 1999). In the SPE procedure, the choice of the appropriate sorbent is a critical factor to obtain full recovery and a high-enrichment factor. Although numerous substances have been applied as solid-phase extraction sorbents, such as C18 silica (Jak et al., 2004), polymeric sorbents (Rao et al., 2004), and polyurethane foam (Lemos et al., 2007), their applicability is often limited only to a number of analytes. Thus, developing new SPE adsorbents is of high value.

Carbon materials are well known for their high adsorption capacity. They have been proven to possess great potential as adsorbents for removing many kinds of environmental pollutants: some examples are activated carbon (Ensafi and Shiraz, 2008), fullerenes (Vallant et al., 2007), carbon nanotubes (CNTs) (Shamspur and Mostafavi, 2009), carbon nanohorn (Zhu et al., 2009), and carbon nanocones/disks (Jimenez-Soto et al., 2009).

Graphene (G) is a new exciting carbon material being investigated today, not only out of academic curiosity but also with potential applications in mind (Rao et al., 2009). It is a two-dimensional material, composed of layers of carbon atoms forming six membered rings. Graphene is the mother of all graphitic forms including zerodimensional fullerenes, one-dimensional carbon nanotubes and three-dimensional graphite (Geim and Novoselov, 2007). Compared with other graphitic forms, graphene possesses extraordinary electronic, thermal, and mechanical properties such as ultrahigh specific surface area, good thermal conductivity, fast mobility of charge carriers, and high values of Young's modulus and fracture strength (Stoller et al., 2008; Lee et al., 2008; Balandin et al., 2008; Bolotin et al., 2008). To date, the unique planar structure of graphene provides tremendous potential applications in many fields. For example, graphene served as filler for the enhancement of mechanical and electrical properties in composite materials (Yang et al., 2009; Watcharotone et al., 2007). Graphene-based materials were also used as sensors for the sensitive and selective detection of biomolecules (Lu et al., 2009; Chang et al., 2010; Shan et al., 2009), and graphene/polymer composite is a candidate for supercapacitors because of their high specific capacitance and good cycling stability (Zhang et al., 2010).

Exceptional properties make graphene a superior candidate as an adsorbent for SPE. Firstly, graphene has a large specific surface area (theoretical value 2630 m^2/g [Stoller et al., 2008]), suggesting a high sorption capacity. Specifically, both sides of the planar sheets of graphene are available for molecule adsorption, whereas for CNTs and fullerenes, steric hindrance may exist when molecules access their inner walls. Secondly, graphene can be easily modified with functional groups, especially via graphene oxide which has many reactive groups (Park and Ruoff, 2009). Functionalization may further enhance the selectivity of SPE. Thirdly, CNTs usually contain trace amounts of metallic impurities that come from the metal catalysts used in their synthesis. These impurities may have negative effects on the applications of CNTs (Banks et al., 2006; Pumera and Miyahara, 2009). Graphene, on the other hand, can be synthesized from graphite without the use of metal catalysts, thus obtaining pure material. Fourthly, despite being chemically reduced, graphene sheets still have some hydrophilic groups such as hydroxyl and carboxyl groups. These hydrophilic groups can improve the water-wettability of graphene and enhance the retention and elution of polar compounds (Liu et al., 2011). These features make graphene very attractive as an adsorbent material.

Despite their potential advantages, less attention has been paid to the SPE applications of graphene. Dong et al. (Dong et al., 2010) and Tang et al. (Tang et al., 2010) recently reported the use of graphene as a matrix or probe for matrix-assisted or surface-enhanced laser desorption ionization time-of-flight mass spectrometry. In these reports, graphene as adsorbent or extraction material was dispersed into the sample solution; centrifugation or filtration followed to separate or retrieve the tiny graphene from dispersion (Dong et al., 2010; Schniepp et al., 2006). However, the graphene sheets were difficult to isolate completely from the dispersions even by high-speed centrifugation because of the presence of miniscule sheets of graphene. Furthermore, the procedure is quite troublesome, tedious, and offers inefficient retrieval of graphene.

To ease the retrieval procedure, the SPE using graphene as the absorbent in a column combined with flame atomic absorption spectrometry (FAAS) has been demonstrated by our research group (Wang et al., 2012). We extend its application to other inorganic analyses. 1-(2-Pyridylazo)-2-naphthol (PAN), a chelating agent which forms stable complexes with a number of metals and has found numerous applications in trace element separation and pre-concentration methods (Narin and Soylak., 2003; Shokoufi et al., 2007), was used to extract Co (structure of the Co-PAN complex is shown in Fig. 1). What is more, it possesses a benzene ring structure. Based on this, the Co-PAN is considered to have formed a strong π-stacking interaction with graphene when the sample solution passes through the column during which the Co-chelate is retained. The factors influencing the efficiency of SPE and FAAS determination were systematically studied. The proposed method has been applied for the determination