



# Graphene oxide covalently modified with 2,2'-iminodiacetic acid for preconcentration of Cr(III), Cu(II), Zn(II) and Pb(II) from water samples prior to their determination by energy dispersive X-ray fluorescence spectrometry

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## ABSTRACT

A novel adsorbent, graphene oxide modified with 2,2'-iminodiacetic acid (GO-IDA), was synthesized by nucleophilic substitution of dimethyl-2,2'-iminodiacetate hydrochloride to the surface of graphene oxide (GO). It was applied in the dispersive micro-solid phase extraction (DMSPE) for the simultaneous preconcentration of selected heavy metal ions from water samples prior to determination by Energy Dispersive X-Ray Fluorescence Spectrometry (EDXRF). The experiments show that at pH 6.5 GO-IDA can be used for quantitative adsorption of Cr(III), Cu(II), Zn(II) and Pb(II) ions from water samples. The adsorption capacities of GO-IDA towards Cr(III), Cu(II), Zn(II) and Pb(II) ions are found to be 117.1, 108.4, 119.6, and 80.7 mg g<sup>-1</sup>, respectively. The experimental data are fitted better by the Langmuir model than by the Freundlich model. Under optimal preconcentration conditions the linear response between analyte concentration and fluorescence radiation intensity was observed within 1–200 ng mL<sup>-1</sup> for Cr(III) and Cu(II), 1–140 ng mL<sup>-1</sup> for Zn(II), and 1–100 ng mL<sup>-1</sup> for Pb(II) ions. The uncertainty of the developed method does not exceed 4.3%. The detection limits are 0.11, 0.06, 0.07 and 0.08 ng mL<sup>-1</sup> for Cr(III), Zn(II), Cu(II) and Pb(II), respectively. The enrichment factors obtained for the 50 mL sample volume are in 450–1465 range. The DMSPE-EDXRF procedure was applied for the determination of Cr(III), Cu(II), Zn(II) and Pb(II) ions in different types of water samples. The accuracy of the procedure was verified by the analysis of Certified Reference Material: NIST 1640a (Trace elements in natural water).

## 1. Introduction

Water is one of the most valuable biosphere component and although it represents almost 70% of the Earth's surface, only about 30% of the total amount is present in the pure form indispensable to the maintenance of the Earth life [1]. The chemical composition of natural waters depends on many factors including natural processes, anthropogenic activities and atmospheric input [2,3]. Generally, all components existing in water can be classified into six categories: main ions, dissolved gases, biogenous substances, organic substances, microelements and pollutants [4]. From the above-mentioned groups pollutants are a matter of a great concern now, because they affect the normal development of plants and animals. Among them, heavy metals play a

crucial role, because they are not biodegradable and can be accumulated in tissues causing several diseases and disorders. Therefore, their concentration in water should be constantly monitored. Having in mind that metal ions are usually present in water at trace or ultra-trace levels and their direct determination can be hampered by matrix interferences, a preliminary separation and/or preconcentration is usually necessary.

Since its introduction by Pawliszyn [5], solid-phase microextraction (SPME), has gained an unremitting attention due to its simplicity, low costs, the facility to handle large volume samples, rapid phase separation, low consumption of organic solvents, high enrichment factors, the possibility of combining off- and on-line systems with different analytical techniques and a variety of commercially available adsorbents [6].

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In recent years, classical adsorbents used in SPME e.g. ion-exchange resins, chelate resins, cellulose, silica gels or activated charcoal have been gradually replaced by various types of nanosorbents including carbon based nanomaterials such as single-walled and multi-walled nanotubes, graphene and graphene oxide. Such popularity of nano-sized materials results from their large surface area and high adsorption capacity, chemical stability and excellent efficiency [7–10].

Graphene oxide (GO), firstly reported in 1860 by Brodie [11], consists of a hexagonal ring-based carbon honeycomb structure having both  $sp^2$ -hybridized carbon atoms and  $sp^3$ -hybridized carbons bearing hydroxyl and epoxy functional groups on either side of the sheet, whereas the sheet edges are mostly decorated by carboxyl and carbonyl groups [12,13]. For that matter GO is often simplistically acknowledged as a graphene sheet bonded to oxygen groups [14]. These functional groups are responsible for binding different types of molecules and metal ions. When metal ions are bound alone electron pair located on the each oxygen atom is involved. Considering the possibility of chemical bonds formation, large surface area and accessibility of both nanosheet sides to adsorption GO displays an impressive adsorption capacity towards metal ions. However, due to its unselectivity the adsorption can be hampered by the competition of metal ions to the same adsorption sites. Such problem can be omitted by modification of GO with metal nanoparticles, different molecules, or by introduction onto its surface a diversity of functional groups [15–18]. Generally, functionalization alters chemical reactivity and as a consequence its selectivity. Moreover, adsorbents of desired properties can be synthesized. Methods used for the modification of GO can be classified as covalent and noncovalent ones. The first one are based on the formation of chemical bonds by nucleophilic or electrophilic substitution, condensation or addition reaction. Van der Waals forces, hydrogen bonding and  $\pi$ - $\pi$  stacking interactions are responsible for noncovalent bonding. In both cases the presence of defects and oxygen containing functional groups on GO surfaces facilitate modifications [18]. However, adsorbents obtained in the covalent way are more stable and can be used repeatedly, so this approach has a greater potential. Recently, some GO-based adsorbents, synthesized in covalent way, have been reported for the adsorption of various metal ions, i.e. Pb(II) [19–26], Cu(II) [19,21,22,25–30], Co(II) [19,22,31], Fe(II) [25], Zn(II) [19,25,30], Cd(II) [22,26,31,32], Au(III) [33], Pd(II) [33], Ni(II) [19], Cr(III) [25,30], Cr(VI) [34], Mn(II) [26,35], Hg(II) [36], or speciation of As(III) and As(V) [22].

Herein, covalent modification of graphene oxide (GO) with 2,2'-iminodiacetic acid (IDA) was utilized to create a novel adsorbent, referred as GO-IDA. The obtained nanomaterial was characterized by Fourier Transform Infrared Spectroscopy (FTIR), Raman Spectroscopy, X-Ray Photoelectron Spectroscopy (XPS), Scanning Electron Microscopy (SEM), and Transmission Electron Microscopy (TEM). Moreover, the zeta potential ( $\zeta$ ) of GO-IDA aqueous suspensions at different pH values was also measured. To assess the usefulness of GO-IDA as a solid adsorbent, a procedure based on dispersive micro-solid phase extraction (DMSPE) for the preconcentration of selected heavy metal ions from water samples prior to their determination by Energy Dispersive X-Ray Fluorescence Spectrometry (EDXRF) was applied. All parameters affecting the preconcentration procedure, i.e. pH of the solution, adsorbent mass, adsorption time and sample volume, were carefully studied. The developed DMSPE-EDXRF procedure was applied to the determination of the analyte ions in different types of water samples. The accuracy of the method was verified by the determination of Cr(III), Cu(II) Zn(II) and Pb(II) in certified material NIST 1640a (Trace elements in natural water).

## 2. Experimental

### 2.1. Chemicals and solutions

Stock solutions ( $1 \text{ mg mL}^{-1}$  of Cr(III), Co(II), Mn(II), Ni(II), Cu(II),

Zn(II) and Pb(II)), nitric acid (65%, Suprapur®) and ammonium hydroxide solution (25%, Suprapur®) were purchased from Merck (Darmstadt, Germany). Salts used for the interferences studies, 2,2'-iminodiacetic acid (IDA), potassium permanganate, sulphuric acid and ethanol were purchased from POCh (Gliwice, Poland). Thionyl chloride ( $\text{SOCl}_2$ ) was purchased from Acros Organics. Tetrahydrofuran (THF) and *N,N*-dimethyl-formamide (DMF) were purchased from Chempur (Piekary Śląskie, Poland). Graphite powder (325 mesh) was purchased from Alfa Aesar (Karlsruhe, Germany). Trace elements in natural water Certified Material (NIST 1640a) was purchased from National Institute of Standards and Technology (250 mL, certified issue date: 08 June 2010, the certification is valid until 05 August 2020, Gaithersburg, USA). The pH of the analyzed solutions was adjusted with  $0.1 \text{ mol L}^{-1}$   $\text{HNO}_3$  and  $0.1 \text{ mol L}^{-1}$   $\text{NH}_3 \cdot \text{H}_2\text{O}$ . The suspension of modified graphene oxide ( $1 \text{ mg mL}^{-1}$ ) was prepared using high purity water. Before use, the GO-IDA suspension was sonicated for 15 min in order to obtain a homogeneous suspension. High purity water obtained from a Milli-Q system (Millipore, Molsheim, France) was used during the experiments.

### 2.2. Instrumentation

Structural measurements were performed using FTIR Nicolet Magna 560 spectrometer, PHI 5600 Physical Electronic Spectrometer, JEOL-5410 SEM and JEOL JEM 3010 TEM, JSM-5410 scanning microscope equipped with an energy dispersion X-ray spectrometer (EDS), and ZetaSizer Nano (Malvern Instruments). The EDXRF measurements were carried out using Epsilon 3 (PANalytical, Almelo, The Netherlands). Recovery studies as well as adsorption capacity of GO-IDA were conducted using SpecroFMS16a spectrometer with the excitation in the ICP plasma (Spectro Analytical Instruments). Details concerning the apparatus applied in this study are given in the Appendix A. Supplementary data.

### 2.3. Synthesis of dimethyl-2,2'-iminodiacetate hydrochloride

13.31 g of 2,2'-iminodiacetic acid was suspended in 150 mL of dry methanol under argon atmosphere using magnetic stirrer. The obtained suspension was cooled in an ice bath and 29 mL of freshly distilled thionyl chloride was added in drops under argon atmosphere. After that, the cooling bath was removed and stirring was continued at a room temperature overnight under argon atmosphere. The resulting mixture was concentrated in vacuum to approximately 10% of the initial volume and the precipitate was filtered, washed with 40 mL of diethyl ether and dried under vacuum to obtain a white solid (13.05 g, 81%). The structure of dimethyl-2,2'-iminodiacetate hydrochloride was confirmed by  $^1\text{H}$  NMR (400 MHz,  $\text{D}_2\text{O}$ )  $\delta$ : 4.04 (s, 4H), 3.75 (s, 6H) and  $^{13}\text{C}$  NMR (101 MHz,  $\text{D}_2\text{O}$ )  $\delta$ : 167.4, 53.5, 47.1.

### 2.4. Synthesis of GO-IDA

Graphene oxide used for GO-IDA synthesis was obtained by modified Hummers' method [37]. A mixture of 1 g of GO, 160 mL of  $\text{SOCl}_2$  and 5 mL of THF was stirred at  $70^\circ\text{C}$  under argon atmosphere for 24 h. After that an excess of  $\text{SOCl}_2$  was removed under reduced pressure (ca. 0.3 atm) at  $50^\circ\text{C}$  using a conventional rotary evaporator. Next, 10 g of dimethyl-2,2'-iminodiacetate hydrochloride in 100 mL of DMF was added to the suspension and stirring was continued under Ar atmosphere at  $70^\circ\text{C}$  for 48 h. The solid residue was separated by centrifugation and washed 10 times with ethanol-water mixture (1:1) in order to remove an excess of dimethyl-2,2'-iminodiacetate hydrochloride. Each time, the product was redispersed by sonication (15 min) and collected by centrifugation (5000 rpm, 5 min). The obtained solid was dried at  $60^\circ\text{C}$ . In order to perform hydrolysis 80 mL of  $2 \text{ mol L}^{-1}$  HCl was added to the solid and the suspension was stirred under Ar atmosphere at  $50^\circ\text{C}$  for 10 h. The synthesized GO-IDA was then centrifuged (5000 rpm, 5 min), washed with water to neutral pH and dried

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