Alumina/nano-graphite composite as a new nanosorbent for the selective adsorption, preconcentration, and determination of chromium in water samples by EDXRF

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Abstract

Obtaining new nanocomposites with sorption properties towards chromium is highly important not only from the environmental point of view but also for developing eco-friendly methods of chromium determination. The potential use of aluminum oxide-coated nano-graphite (Al 2O 3/nano-G) as a new nanosorbent in ultrasound-assisted dispersive micro-solid-phase extraction (DMSPE) for rapid speciation of trace chromium(III) and chromium(VI) ions in natural water was evaluated. In the developed method, the crucial issue is the new nanocomposite synthesized by coating alumina on a nano-graphite surface with sorption properties. Structural researches of the nanocomposite were carried out by scanning electron microscopy (SEM), powder X-ray diffraction (XRD), and Raman spectroscopy. Maximum adsorption capacity of Al 2O 3/nano-G towards Cr(III) was 32.8 mg g⁻¹. The influence of the method’s factors like pH, sample volumes, contact time, coexisting ions, and humic acid on the recovery of chromium was examined. The nanocomposites have been found to be stable and effective as a sorbent in water with high concentrations of selected cations and anions present in water as well as in water of various pH. Al 2O 3/nano-G is selective for Cr(III) in presence of Cr(VI). Cr(III) was determined by the developed method, total Cr after reduction of Cr(VI) to Cr(III), and Cr(VI) was calculated as the difference between total Cr and Cr(III). After sorption, the nanocomposite with chromium was collected on 5-mm diameter filters and analyzed by energy-dispersive X-ray fluorescence spectrometry (EDXRF) to determine the chromium concentration. The method was characterized by correlation coefficient 0.999, limit of detection (LOD) 0.04 ng mL⁻¹, and relative standard deviation (RSD) 3.5%. Al 2O 3/nano-G combined with proposed DMSPE/EDXRF was verified by analysis of certificate reference material of natural water (NIST 1640a).

Keywords Preconcentration · Speciation · Trace analysis · Nanosorbent · Environmental samples · Sorption

Introduction

The interest in chromium speciation originates from widespread use of this metal in various industries such as chemical, metallurgical, and refractories. Thus, large quantities of chromium compounds are discharged in solid, liquid, and gaseous wastes into the environment and can have potentially adverse biological and ecological effects. The two widespread oxidation states of Cr are present in the environment, i.e., Cr(III) and Cr(VI). They are drastically different in chemical and biochemical reactivity and physicochemical properties [1]. Cr(III) is considered to be a trace element essential for the proper functioning living organisms, but in a significant concentration can cause adverse effects because of its high capability to coordinate various organic compounds, whereas Cr(VI) is considered exerting toxic effects on biological systems. It was found that exposure to hexavalent Cr compounds can lead to a variety of clinical problems [2]. Thus, a detailed knowledge of each species rather than the total chromium level is required to properly evaluate its toxicological effects, and distribution in the environment. The concentration of chromium in environment is controlled and observed by the World Health Organization (WHO) [3] and the Environmental Protection Agency (EPA) [4]. WHO and EPA have

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established an upper concentration limit for chromium in drinking water, which equals 50 ng mL\(^{-1}\) and 100 ng mL\(^{-1}\), respectively.

The literature proposes a lot of methods to oxidation and/or reduction of chromium before the removal/separation. The Cr(III) ions can be oxidized by potassium permanganate solution (KMnO\(_4\)) \([5, 6]\), hydrogen peroxide (H\(_2\)O\(_2\)) \([7, 8]\), or potassium peroxodisulfate (K\(_2\)S\(_2\)O\(_8\)) in acid solution \([9]\). Many methods allowing reducing Cr(VI) ions are also shown in the literature. The concentrated sulfuric acid (H\(_2\)SO\(_4\)) with ethanol (C\(_2\)H\(_5\)OH) \([10, 11]\), hydroxylamine hydrochloride (NH\(_2\)OH · HCl) solution \([12–14]\), or hydrochloric acid (HCl) solution with C\(_2\)H\(_5\)OH \([15]\) has played a good role in complete reduction of Cr(VI).

For determination of trace amounts of chromium in different materials, oxidized multiwalled carbon nanotubes (MWCNTs) \([14]\), MWCNTs modified with the anionic exchange tricaprylmethylammonium chloride (Aliquat 336) \([16]\), graphene oxide (GO) \([11]\), graphene oxide decorated with triethylenetetramine-modified magnetite (mf-GO) \([17]\), and graphene (G) \([18]\) were applied. The trace amount of chromium ions was preconcentrated using solid-phase extraction (SPE) \([18]\) and dispersive magnetic SPE \([17]\) combined with flame atomic absorption spectrometry (FAAS), dispersive micro-solid-phase extraction (DMSPE) combined with total reflection X-ray fluorescence (TXRF) \([16]\), and energy-dispersive X-ray fluorescence spectrometry (EDXRF) \([11]\). Several carbon sorbents have also high affinity for both chromium and other heavy metals. Oxidized MWCNTs \([19]\), 3-(2-aminoethylamino)propyltrimethoxysilane (AAPTS) functionalized MWCNTs \([6]\), Schiff base-chitosan-grafted MWCNTs (S-CS-MWCNTs) \([20]\), nano-graphite \([21]\), GO nanosheets \([22]\), and GO connected with 2-(5-bromo-2-pyridylazo)-5-diethylaminophenol (5-Br-PADAP) \([23]\) have found analytical application in the sorption and determination not only of Cr(III) and Cr(VI) but also of Mn(II), Fe(III), Co(II), Ni(II), Cu(II) Pb(II), As(V), Se(VI), and V(V). The previous studies have shown that alumina supported on graphene oxide (Al\(_2\)O\(_3\)/GO) can be successfully used for preconcentration of As(V) and Cr(III) \([24]\).

In this work, the alumina was supported on nano-graphite to obtain Al\(_2\)O\(_3\)/nano-G composite suitable for selective sorption of chromium in both batch and under flow conditions. Thanks to microscopy and spectroscopy researches, Al\(_2\)O\(_3\)/nano-G composite structure was confirmed and characterized. The maximum adsorption capacity of the new nanosorbent was evaluated by Langmuir isotherm model. Al\(_2\)O\(_3\)/nano-G composite was applied in DMSPE combined with EDXRF. The advantage of this methodology over ICP-OES, ICP-MS, and FAAS is the possibility of direct determination of analyte onto sorbent without elution. Thus, errors connected with contamination of sample or losses of analyte are eliminated and time of sample preparation is shortened. The preconcentration of Cr(III) by Al\(_2\)O\(_3\)/nano-G can be performed within 5 min. The obtained samples are durable; thus, they can be stored and analyzed many times as well as can be used in further research. Analytes can be also determined after elution from nanocomposite, using alternative techniques. Application of Al\(_2\)O\(_3\)/nano-G in DMSPE/EDXRF method allows for direct determination of trace amounts of Cr(III) in environment water samples. The developed methodology is environmentally friendly and non-time-consuming.

**Materials and methods**

**Materials**

Chromium stock solution 1 mg mL\(^{-1}\) of Cr(III) and Cr(VI) was purchased from Merck (Darmstadt, Germany); humic acid was purchased from Sigma-Aldrich (Steinheim, Germany); graphene nanopowder 8 nm (purity 99.99% and the flakes size 8 nm) was purchased from graphene supermarket (New York, USA); nitric acid (65%, Suprapur®), ammonium hydroxide solution (25%, Suprapur®,) ethanol (96% p.a.), sulfuric acid (96% p.a.), Triton X-100 (p.a.), chromium(III) nitrate nanohydrate (p.a.), sodium nitrate (p.a.), potassium nitrate (p.a.), calcium nitrate tetrahydrate (p.a.), magnesium nitrate hexahydrate (p.a.), iron(III) nitrate nanohydrate (p.a.), aluminum nitrate nanohydrate (p.a.), buffer solution (pH 4.00 ± 0.05 and pH 7.00 ± 0.05), and the Munktell membrane filters of thickness 176 μm (no. 391) were purchased from Avantor Performance Materials Poland S.A. (Gliwice, Poland). Standard solutions were diluted with high-purity water obtained from Milli-Q system (Millipore, Molsheim, France). Certified Reference Material (natural water 1640a) was purchased from National Institute of Standards and Technology (Gaithersburg, USA).

**Apparatus**

The microstructural observation of the Al\(_2\)O\(_3\)/nano-G was on a JOEL-7600F scanning electron microscope (SEM) (Oregon, USA) equipped with the Oxford X-ray energy-dispersive spectrometer (EDS). Powder X-ray diffraction data (XRD) (PANalytical, Almelo, The Netherlands) were collected on X’Pert PRO X-ray diffractometer with PIXcel ultrafast line detector and Soller slits for Cu K\(_{\alpha}\) radiation. The measurements were done in Bragg-Brentano geometry.

The Raman spectra (Renishaw, New Mills, Wotton-under-Edge Gloucestershire, UK) were measured at room temperature using Renishaw InVia Raman spectrometer equipped with confocal DM 2500 Leica optical microscope, a thermoelectrically cooled Ren Cam CCD detector and a diode laser operating at 830 nm.
The EDXRF spectra were measured by energy-dispersive X-ray fluorescence spectrometer Epsilon 3 (PANalytical, Almelo, The Netherlands) with the Rh target X-ray tube with 50-μm Be window and max. power of 9 W. The spectrometer is equipped with thermoelectrically cooled silicon drift detector (SDD) with 8-μm Be window and resolution of 135 eV at 5.9 keV. The spectrometer is equipped with spinner and five primary filters that can be selected to improve measuring conditions for determined elements. The measurement conditions are 20 kV, 450 μA, Al filter of 200-μm thickness, air atmosphere, and 300 s of measure time. The samples were packed in mylar foil of 6-μm thickness.

ICP-OES (Spectro Analytical Instruments GmbH, Kleve, Germany) measurements were performed using a SpectroBlue FMS16 spectrometer with inductively coupled plasma (ICP) excitation (Spectro Analytical Instruments) and a charge-coupled-device detector. The following operation parameters were used for measurements: plasma power—1.45 kW; coolant gas—Ar, 12 L min⁻¹; auxiliary gas—Ar, 1 L min⁻¹; nebulizer gas—Ar, 1 L min⁻¹; nebulizer pressure—3.2 bar; nebulizer-cross-flow type; sample uptake rate—2 mL min⁻¹; wavelength—267.716 nm for Cr.

Ultrasonication bath with heating, EMAG, Emmi 20 HC model was purchased from EMAG Poland (Juszczyn, Poland); ultrasonic power, 150 W; working range of ultrasonic power, 50–100%; heating power, 200 W; working range of temperature, 20–80 °C; frequency, 45 kHz; and maximum volume, 1.4 L.

**Synthesis of Al₂O₃/nano-G composite**

Al₂O₃/nano-G composite was synthesized as follows: 5 g of Al(NO₃)₃ · 9H₂O, 300 mg of Triton X-100, and 1 g of high-purity graphene nanosheets were sonificated in 100 mL of water for 2 h. The black suspension was dried at 80 °C for 10 h and then heated at 500 °C for 2 h to obtained Al₂O₃ nanoparticles supported on nano-graphite (Al₂O₃/nano-G) [25].
Preparation of Al₂O₃/nano-G suspension

Two hundred fifty milligrams of Al₂O₃/nano-G was placed in 50-mL flasks and filled with high-purity water up to the mark. Directly before using, the suspension of the nanocomposite was placed in an ultrasonic bath for 30 min in order to homogenize the dispersion.

Preconcentration procedure

Two hundred-microliter aliquot of the suspension of Al₂O₃/nano-G (1 mg) was added into 25 mL of water sample. Then, the 0.1 mol L⁻¹ HNO₃ and 0.1 mol L⁻¹ NH₃aq were used to adjust the pH of the samples. Then, the sample was stirred for 5 min and passed through membrane filter in 2 min using the filtration assembly of 5-mm diameter. After drying for 5 min, the sample was measured by EDXRF.

The total time of sample preparation did not exceed 15 min. But using a multi-position magnetic stirrer and two vacuum filtration kits, a series of 10 samples in 30 min can be simultaneously prepared.

Batch adsorption

The batch adsorption experiments were carried out with 1 mg of Al₂O₃/nano-G, 25 mL of Cr(III) solutions with specified concentration, and pH. The pH values of the suspensions of Al₂O₃/nano-G and Cr(III) were adjusted with HNO₃ and NH₃aq solutions. The suspensions were stirred for 90 min to achieve adsorption equilibrium. Next, the suspensions were filtrated through membrane filters. The amount of Cr(III) ions adsorbed on Al₂O₃/nano-G (mg g⁻¹) was calculated from the difference between the initial concentration C₀ (mg L⁻¹), and equilibrium concentration Cₑ determined in filtrate by the ICP-OES spectrometry: 

\[ q_{\text{max}} = (C_0 - C_e)V/m_{\text{adsorbent}}, \]

where V is the volume of the suspension, and m_{adsorbent} is the mass of Al₂O₃/nano-G. The recovery is given as

\[ \text{Recovery\%} = 100\%\left(\frac{C_0 - C_e}{C_0}\right). \]
Results and discussion

Structural research

The synthesized Al$_2$O$_3$/nano-G was characterized by SEM. Figure 1a shows a SEM image of Al$_2$O$_3$/nano-G composite. As can be seen, the alumina particles are shown on the surface of the thin layer of G nanosheets. The G nanosheets are semi-transparent suggesting their few-layer nature. Both the distribution maps of C, Al, and O elements (see Fig. 1b–d) in Al$_2$O$_3$/nano-G composite as well as the good correlation between distributions of aluminum and oxygen on the surface of nanocomposite confirm the presence of Al$_2$O$_3$ nanoparticles on the surface of nano-graphite.

Al$_2$O$_3$/nano-G was also characterized by XRD and Raman spectroscopy. Figure 2a presents XRD pattern of Al$_2$O$_3$/nano-G. The pattern for Al$_2$O$_3$/nano-G is characteristic of graphite; there are not any traces of crystallized Al$_2$O$_3$. The most pronounced graphite peak at 20 = 26.5° corresponds to coherently scattering hexagonal carbon layers with a d$_{002}$ spacing of 3.36 Å. The diffractogram does not contain discrete patterns which could expose the presence of crystalline entities, including Al$_2$O$_3$. The absence of peaks for Al$_2$O$_3$ phase is due to the amorphous texture [26]. Instead, a plain background is recorded, with high low-angle intensity decreasing at higher theta angles. It resembles simulated XRD patterns for nano-sized, single layers of carbon structures [27].

The Raman spectrum of Al$_2$O$_3$/nano-G (see Fig. 2b) is characteristic of the nano-graphite. It consists of the intense G peak, at around 1582 cm$^{-1}$, that originates from the $E_{2g}$ vibrational mode of ordered in-plane sp$^2$ carbons, and two, broad, and much less intense D and D' bands at 1358 and 1621 cm$^{-1}$, related to the disorder of edge carbons [28]. The intensity ratio $I_D/I_G$ is a measure of the disorder [29]. In Al$_2$O$_3$/nano-G, the $I_D/I_G$ is equal to 0.51 indicating the prominent disorder of the G nanosheets. The main source of the disorder comes from the small size of the G nanosheets, as it is indicated by the XRD and the presence of the oxygen functional groups as well as the number of areas of sp$^2$ carbons with an alternating pattern of single-double carbon bonds [30] that generate huge blue shift of the G band to 1613 cm$^{-1}$. The absence of peaks related to Al$_2$O$_3$ confirms its amorphous structure.

pH effect

The effect of pH of aqueous solutions was investigated between 1.0 and 9.0 for a wide range of metal ions including

**Table 1** Effect of coexisting ions and HA on adsorption process using Al$_2$O$_3$/nano-G as a sorbent in DMSPE/EDXRF procedure (experiment conditions: 1 mg of Al$_2$O$_3$/nano-G, 25 mL of sample volume, 10 ng mL$^{-1}$ of Cr(III), pH = 6.5, adsorption time = 5 min)

| Interferent | Concentration ($\mu$g mL$^{-1}$) | Added as | Interferent/adsorbed ion ratio | Recovery (% ± RSD) |
|-------------|---------------------------------|----------|-------------------------------|---------------------|
| Na$^+$      | 200                             | NaNO$_3$ | 20,000                        | 95.48 ± 0.65        |
| K$^+$       | 200                             | KNO$_3$  | 20,000                        | 105.36 ± 0.09       |
| Mg$^{2+}$   | 200                             | Mg(NO$_3$)$_2$·6H$_2$O | 20,000 | 95.61 ± 0.20 |
| Ca$^{2+}$   | 200                             | Ca(NO$_3$)$_2$·4H$_2$O | 20,000 | 94.65 ± 0.57 |
| Fe$^{3+}$   | 10                              | Fe(NO$_3$)$_3$·9H$_2$O | 1000  | 75.67 ± 0.22 |
|             | 5.0                             |          | 500                            | 82.18 ± 0.82        |
|             | 2.5                             |          | 250                            | 96.75 ± 0.89        |
| NO$_3^-$    | 800                             | KNO$_3$  | 80,000                        | 93.25 ± 1.14        |
| PO$_4^{3-}$ | 1.0                             | Na$_3$PO$_4$·12H$_2$O | 100 | 91.98 ± 1.37 |
| SO$_4^{2-}$ | 300                             | Na$_2$SO$_4$ | 30,000 | 100.16 ± 1.57 |
| Cl$^-$      | 400                             | NaCl     | 40,000                        | 65.12 ± 1.08        |
|             | 300                             |          | 30,000                        | 87.09 ± 0.42        |
|             | 200                             |          | 20,000                        | 93.92 ± 0.48        |
| HA          | 5.0                             | Humic Acid | 500   | 80.62 ± 0.56 |
|             | 4.0                             |          | 400                            | 85.07 ± 0.32        |
|             | 3.0                             |          | 300                            | 94.73 ± 1.68        |
Heavy metal ions. Figure 3 presents relationship between adsorption percentage of multivalent ions, such as Cr(III), Cr(VI), As(III), As(V), Se(IV), and Se(VI) (Fig. 3a) as well as mainly divalent ions, such as Mn (II), Ni(II), Cd(II), Pb(II), Co(II), Cu(II), and Zn(II) and also trivalent ions: Fe(III), Bi(III) (Fig. 3b), and solution pH. As can be seen, Al₂O₃/nano-G shows selective and high affinity for Cr(III) ions. In the acid solution up to pH 3.0, the adsorption percentage is near 20%. Between pH 4.0 and pH 6.5, the adsorption percentage increases and, at pH 6.5, Al₂O₃/nano-G achieved the maximum adsorption (95%). Above pH 6.5 and in the basic solution, adsorption percentage of Cr(III) remains at the high level. In the case of Cr(VI) ions, Al₂O₃/nano-G shows the maximum adsorption percentage (25%) in the range of pH 6.0–7.0. At pH < 6.0 and pH > 7.0, Cr(VI) ions are poorly adsorbed by Al₂O₃/nano-G with adsorption percentage below 20%. The following Cr(III) species in aqueous solution predominate: Cr³⁺ (pH ≤ 5.0), Cr(OH)₂⁺ and CrOH²⁺ (pH ≈ 4.0–6.5), and Cr(OH)₃ (pH > 7.0).

Other metal ions such as As(III), As(V), Se(IV), Se(VI), Mn(II), Fe(III), Ni(II), Cu(II), Zn(II), Cd(II), Pb(II), and Bi(III) are not quantitatively adsorbed by Al₂O₃/nano-G from the solution of pH ≤ 8. Pb(II), Cu(II), and Fe(III) are adsorbed with satisfactory results (near 100%), but only in strong basic solution (pH ≥ 8). The adsorption percentages of Pb(II), Cu(II), and Fe(III) at pH 6 were ca. 55%, 55%, and 70%, respectively. The adsorption percentage for As(V) being about 40% in the range of pH 4.0–6.0 is not enough to preconcentration of trace amounts of these ions. On the other hand, sorption study at pH 9.0, where the adsorption percentage was the highest for Fe(III), Co(II), Ni(II), Cu(II), Zn(II), Cd(II), Pb(II), and Bi(III), cannot be recommended due to the precipitation of metal as, e.g., hydroxides. Finally, taking into consideration both the high adsorption of metal ions and the prevention of the precipitation of metal hydroxides, subsequent experiments and analysis of a real sample were performed only for Cr(III) at a pH of 6.5.

### Adsorption capacity

The adsorption capacity of Al₂O₃/nano-G for Cr(III) ions was investigated using Langmuir [31, 32] and Freundlich [33] isotherms. Langmuir isotherm is described by q_max—the maximum amount of metal ions adsorbed per unit weight of sorbent (Al₂O₃/nano-G) achieving at the high equilibrium ion concentration (mg g⁻¹)—and K_L—the constant related to the free energy of adsorption (L g⁻¹). Freundlich isotherm is described by K_F and n, Freundlich constant related to the adsorption capacity (mg¹⁻ⁿ Lⁿ⁻¹ g⁻¹), and the adsorption intensity, respectively.

\[
q_e = q_{max} \frac{K_L C_e}{1 + K_L C_e}
\]

\[
q_e = K_F C_e^{1/n}
\]

Isotherm parameters were obtained by fitting the adsorption equilibrium data to the isotherm models. The following results for Langmuir and Freundlich isotherms are obtained: q_max = 32.8 mg g⁻¹, K_L = 14.9 L g⁻¹, R = 0.9339, K_F = 28.7 mg¹⁻ⁿ Lⁿ⁻¹ g⁻¹, n = 6.68, R = 0.9123. Because the adsorption isotherms are fitted better by the Langmuir model than by the Freundlich model, a chemical adsorption process is suggested. Langmuir and Freundlich isotherms are presented in Fig. 4.

### Effect of contact time and sample volume

The effect of contact time combined with sample volume on the adsorption recovery of Cr(III) ions on Al₂O₃/nano-G was studied in the range of 5–120 min and 10–500 mL, respectively. The obtained results are presented in Fig. 5. In the range sample volume from 10 to 100 mL, Cr(III) ions were adsorbed with recovery above 90% in the whole studied range of time (5–120 min). For the samples of 250 mL and 500 mL, the recoveries went down step by step. For a sample of 250 mL volume, recoveries decreased from 75 to 65% depending on the sorption time for 120 min and 5 min, respectively. For 500 mL of sample volume, the average recovery for time 5–60 min was ca. 20%, but when the time of sorption was 90 min and 120 min, the recoveries increased to 40% and near 70%, respectively. Consequently, DMSPE with Al₂O₃/nano-G as a

| Analyte  | Analytical range (ng mL⁻¹) | Equation (C, ng mL⁻¹) (I, count s⁻¹) | Correlation coefficient (R) | LOD (ng mL⁻¹) | LOQ (ng mL⁻¹) | RMS (ng mL⁻¹) | RSD (%) |
|----------|---------------------------|--------------------------------------|-----------------------------|----------------|----------------|----------------|---------|
| Cr(III)  | 2.0–50                    | I = 4.943C + 1.146                   | 0.9988                      | 0.04           | 0.15           | 0.87           | 3.47    |

Table 2: The parameters characterized DMSPE/EDXRF methodology (n = 3)

| Added (ng mL⁻¹) | Obtained (ng mL⁻¹) | Recovery (%) |
|-----------------|--------------------|--------------|
| Cr(III)         | Cr(VI)             | Cr(III)      | Cr(VI)      |
| 0               | 0                  | < LOD        | < LOD       | – | – | – | – |
| 10              | 0                  | 9.22 ± 0.68  | < LOD       | 92.2 | – | – | – |
| 0               | 10                 | < LOD        | 9.51 ± 0.14 | – | 95.1 | – | – |
| 10              | 10                 | 9.65 ± 1.12  | 9.38 ± 0.90 | 96.5 | 93.8 | – | – |

Table 3: Determination Cr(III) and Cr(VI) in spiked high-purity water
The effect of flow-rate on chromium recovery is shown in Fig. 5. For comparison, the adsorption of Cr(III) ions under flow conditions needs at least 35 min, i.e., five times longer than in the case of DMSPE (5 min).

### Effect of coexisting ions

The influence of coexisting ions on adsorption of Cr(III) on Al₂O₃/nano-G was investigated in the range of 20–200 μg mL⁻¹ for K⁺, Na⁺, Ca²⁺, and Mg²⁺; 0.1–10 μg mL⁻¹ for Fe³⁺; 100–800 μg mL⁻¹ for NO₃⁻; 0.1–1.0 μg mL⁻¹ for PO₄³⁻; 100–300 μg mL⁻¹ for SO₄²⁻; 50–400 μg mL⁻¹ for Cl⁻; and 0.5–5.0 μg mL⁻¹ for humic acid (HA). The results of these investigations are included in Table 1. The maximum studied concentration of Na⁺, K⁺, Mg²⁺, Ca²⁺, NO₃⁻, PO₄³⁻, and SO₄²⁻ ions did not negatively affect the adsorption process of Cr(III) onto Al₂O₃/nano-G. According to WHO [34, 35] and EPA [36] regulations, the maximum concentrations of NO₃⁻, SO₄²⁻, and Cl⁻ in surface waters are in the range 0–18 μg mL⁻¹, 0–250 μg mL⁻¹, and 40–63 μg mL⁻¹, respectively. Tolerance limit of Al₂O₃/nano-G in preconcentration of Cr(III) ions towards abovementioned ions are 45, 1.2, and 3.2 times better. In the groundwater, the concentrations of Mg²⁺, Ca²⁺ [37], Fe³⁺, NO₃⁻ [36], SO₄²⁻ [38], PO₄³⁻, and Cl⁻ [36] are not higher than 100, 100, 2.0, 50, 230, 0.7, and 250 μg mL⁻¹, respectively. Thus, as obtained results show, nanocomposite can be also used in the analysis of groundwater. Cr(III) ions can be also successfully preconcentrated on Al₂O₃/nano-G using DMSPE when the concentrations of Fe³⁺ and HA are 2.5 μg mL⁻¹ and 3.0 μg mL⁻¹, respectively. Concentrations of iron in drinking water are normally less than 0.3 μg mL⁻¹. Big tolerance of the proposed method towards coexisting ions allows applying Al₂O₃/nano-G as a sorbent to determination of chromium in different kinds of water such as ca. drinking and surface water as well as groundwater.

### Table 5

| Water          | Mayor element of matrix (mg L⁻¹) | Major trace element of matrix (μg L⁻¹) | Analyte | Certified concentration (μg L⁻¹) | Determined concentration (μg L⁻¹) | Error (%) |
|----------------|---------------------------------|--------------------------------------|---------|-------------------------------|----------------------------------|-----------|
| NIST 1640a     | Ca (5.615 ± 0.021), Mg (1.0586 ± 0.0041), K (0.5799 ± 0.0023), Si (5.210 ± 0.021), Na (3.137 ± 0.031) | Al (53.0 ± 1.8), As (8.075 ± 0.070), Ba (151.80 ± 0.83), B (303.1 ± 3.1), Cr (40.54 ± 0.30), Co (20.24 ± 0.24), Cu (85.75 ± 0.51), Fe (36.8 ± 1.8), Mn (40.39 ± 0.36), Mo (45.60 ± 0.61), Ni (25.32 ± 0.14), Pb (12.101 ± 0.050), Sr (20.13 ± 0.17), Sr (126.03 ± 0.27), U (25.35 ± 0.27), V (15.05 ± 0.25), Zn (55.64 ± 0.35) | Cr       | 40.54 ± 0.30 | 39.38 ± 0.39 | 2.85      |
Analytical performance

The calibration curve was prepared under optimized conditions based on series of standard solutions including various concentrations of Cr(III) from 2.0 to 50 ng mL$^{-1}$. The characteristic of the method is presented in Table 2. Limit of detection (LOD) was calculated using the formula 

$$\text{LOD} = \left(\frac{3}{k}\right)\left(\frac{B}{t}\right)^{1/2},$$

where $k$ is the sensitivity read from equation (mg mL$^{-1}$ s$^{-1}$), $B$ is the background count rate (counts s$^{-1}$), and $t$ is the counting time (300 s). Limit of quantification (LOQ) was calculated from $\text{LOQ} = 3.3 \cdot \text{LOD}$. The root mean square (RMS) describes the sum of the differences between the values of the standard and calculated concentrations. The method precision was characterized by average relative standard deviation (RSD).

The proposed method can be applied to the simultaneous determination of Cr(III), Cr(VI), and total Cr. The recoveries were examined by spiking water samples with various Cr species. In order to determine total Cr in spiked water samples (see Table 3), the prereduction step using concentrated H$_2$SO$_4$ and ethanol was applied before using the developed methodology. Cr(III) was determined directly using the developed procedure. But the concentration of Cr(VI) was calculated by subtracting the concentration of Cr(III) from total chromium concentration. The results presented in Table 3 show that various species of chromium can be successfully determined in water samples by DMSPE/EDXRF with Al$_2$O$_3$/nano-G as a sorbent.

The developed method was also successfully applied for the determination of trace amounts of chromium ions in different types of drinking water samples, e.g., mineral and tap water. Analyzed water samples were spiked with 7.5 ng mL$^{-1}$ and 15 ng mL$^{-1}$ of Cr(III) ions. Table 4 presents the obtained results showing that the recoveries of enriched chromium (91–107%) are reasonable for trace analysis.

### Analytical application of Al$_2$O$_3$/nano-G

The obtained Al$_2$O$_3$/nano-G composite combined with the developed DMSPE/EDXRF methodology was applied to analysis of certified reference material (CRM) of natural water.

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**Table 6** Comparison of the developed DMSPE/EDXRF methodology with the other recently published procedures based on solid-phase extraction and its miniaturized derivatives

| Procedure | Sorbent | Analyte | Mass of sorbent (mg) | pH | Analytical range (ng mL$^{-1}$) | Final technique | LOD (ng mL$^{-1}$) | RSD (%) | Ref. |
|-----------|---------|---------|----------------------|----|--------------------------------|----------------|-----------------|--------|------|
| MMHSPE$^a$ | Fe$_3$O$_4$/Al$_2$O$_3$ NPs | Cr(III) | 30 | 8.0 | 10–1000 | FAAS | 1.40 | 3.4 | [40] |
| MSPE$^b$ | Fe$_3$O$_4$@ZrO$_2$ NPs | Cr(III) | 50 | 8.0 | 4.0–400 | FAAS | 0.69 | 2.1 | [41] |
| SPE-FI$^c$ | Nb$_2$O$_5$–SiO$_2$ magnetic NPs | Cr(III) | 100 | 8.0 | 1.2–120 | FAAS | 0.34 | 4.6 | [42] |
| MSPE | Fe$_3$O$_4$@SiO$_2$@CTS$^d$ magnetic NPs | Cr(III) | 20 | 9.0 | 0.1–100 | ICP-OES | 0.02 | 4.8 | [39] |
| SPE | Oxidized SWCNTs | Cr(III) | 20 | 3.0 | 0.1–100 | ICP-MS | 0.01 | 2.1 | [43] |
| SPE | Oxidized MWCNTs | Cr(III) | 2.0 | 4.0 | 5.0–200 | FAAS | 1.15 | 1.7 | [14] |
| DMSPE | Aliquat 336$^j$-MWCNTs | Cr(VI) | 5.0 | 2.0 | 10–3000 | TXRF | 3.00 | 11.9 | [16] |
| DMSPE | GO | Cr(III) | 0.5 | 6.0 | 1.0–150 | EDXRF | 0.06 | 1.7 | [11] |
| DMSPE | mf-GO | Cr(III) | 50 | 8.0 | 5.0–100 | FAAS | 1.60 | 3.4 | [17] |
| DMSPE | G | Cr(III) | 30 | 8.0 | 10–1000 | FAAS | 0.50 | 4.3 | [18] |
| DMSPE | Al$_2$O$_3$/GO | Cr(III) | 1.0 | 6.0 | 2.0–50 | EDXRF | 0.11 | 4.0 | [24] |
| DMSPE | Al$_2$O$_3$/nano-G | Cr(III) | 1.0 | 6.5 | 2.0–50 | EDXRF | 0.04 | 3.5 | This work |

$^a$MMHSPE, magnetic mixed hemimicelles solid-phase extraction; $^b$MSPE, magnetic solid-phase extraction; $^c$FI, flow injection system; $^d$CTS, chitosan; $^j$Aliquat 336, the anionic exchanger tricaprylmethylammonium chloride.
NIST 1640a. The results are shown in Table 5. As can be seen, the accuracy of the method is very good, and the calculated error was below 3%. EDXRF spectra (see Fig. 7) confirmed good peak/background ratio for chromium after its preconcentration on Al2O3/nano-G, which results from the excellent sensitivity of the proposed methodology.

Comparison of DMSPE/EDXRF using Al2O3/nano-G with other methods based on solid-phase extraction

In Table 6, recently published methodologies used for determination of trace amount of chromium ions were compared with the developed methodology. As can be noticed, the different solid-phase extraction procedures and its miniaturized derivatives play an important role in the preconcentration of trace and ultratrace amount of chromium. The advantage of the developed methodology is a fact that only 1 mg of Al2O3/nano-G is enough to preconcentrate trace amount of chromium ions. Meanwhile, according to Table 6, the method using Fe2O3@SiO2@CTS magnetic nanoparticles [39], Fe3O4/Al2O3 [40], Fe2O3@ZrO2 [41], and Nb2O5–SiO2 [42] required 20, 30, 50, and 100 times higher mass of sorbent than synthesized Al2O3/nano-G. Furthermore, the mass of Al2O3/nano-G is less than the mass of the most other carbon sorbents based on modified CNTs and GO. Obtained LOD (0.04 ng mL−1) using the developed method and EDXRF as a measurement technique is better than LOD obtained using FAAS (in the range 0.34–1.60 ng mL−1) [17, 42] and TXRF (3.00 and 2.00 ng mL−1 for aqueous samples) [16]. Al2O3/nano-G combined with DMSPE/EDXRF methodology allowed achieving similar LOD (0.04 ng mL−1) to Fe2O3@SiO2@CTS magnetic nanoparticles connected with MSPE/ICP-OES (0.02–0.03 ng mL−1) [39], oxidized SWCNTs combined with SPE/ICP-MS (0.01–0.02 ng mL−1) [43], and GO with DMSPE/EDXRF (0.06 ng mL−1) [11].

Preconcentration of chromium on Al2O3/nano-G allowed us to decrease the LOD of this element three times in relation to Al2O3/GO nanocomposite used as a sorbent [24].

Conclusion

This paper described a composite based on nano-graphite (G) covered by aluminum oxide (Al2O3) in selective sorption and determination of trace chromium ions in water samples using DMSPE. Al2O3/nano-G combined with the developed methodology played also an important role in speciation of chromium. Thanks to the combination of DMSPE with non-destructive EDXRF as a measurement technique, the chromium ions were determined fast, simple, and effectively in water samples. The advantage of DMSPE/EDXRF methodology is that the elution of analyte is not needed and the Al2O3/nano-G with adsorbed Cr(III) can be analyzed directly. Thus, the developed methodology is eco-friendly and in agreement with the principles of green analytical chemistry. Compared to Al2O3/GO nanocomposite, Al2O3/nano-G is characterized by a much better limit of detection. The LOD achieved by the developed DMSPE/EDXRF procedure (0.04 ng mL−1) is below the highest limit concentration of chromium ions in drinking water according to EPA regulations (100 ng mL−1 of total chromium) [4]. Thus, the method can be recommended to determine chromium ions in water. The accuracy of method (expressed as an error) using certificate material reference NIST 1640a was 3%. The developed method allows determining the trace amount of chromium ions in environmental water samples without unnecessary laboratory work extending time of the analytical procedure and generating additional error sources.

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Compliance with ethical standards

Conflict of interest The authors declare that they have no conflict of interest.

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