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Technical note

Analytical possibilities of different X-ray fluorescence systems for determination of trace elements in aqueous samples pre-concentrated with carbon nanotubes

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ABSTRACT

This study was aimed to achieve improved instrumental sensitivity and detection limits for multielement determination of V, Cr, Mn, Fe, Co, Ni, Cu, Zn, Ga, Se, Pb and Cd in liquid samples by using different X-ray fluorescence (XRF) configurations (a benchtop energy-dispersive X-ray fluorescence spectrometer, a benchtop polarised energy-dispersive X-ray fluorescence spectrometer and a wavelength-dispersive X-ray fluorescence spectrometer).

The preconcentration of metals from liquid solutions consisted on a solid-phase extraction using carbon nanotubes (CNTs) as solid sorbents. After the extraction step, the aqueous sample was filtered and CNTs with the absorbed elements were collected onto a filter paper which was directly analyzed by XRF.

The calculated detection limits in all cases were in the low ng mL^{-1} range. Nevertheless, results obtained indicate the benefits, in terms of sensitivity, of using polarized X-ray sources using different secondary targets in comparison to conventional XRF systems, above all if Cd determination is required.

The developed methodologies, using the aforementioned equipments, have been applied for multielement determination in water samples from an industrial area of Poland.

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1. Introduction

Element determination and quantification in liquid samples is a topic of great interest in many fields. Usually, environmentally important elements are present in water samples in the low $\mu\text{g L}^{-1}$ range, and the analytical procedures used for their determination are usually based on anodic stripping voltammetry and atomic spectrometry [1].

X-ray fluorescence spectrometry (XRF) has been a popular technique for the determination of major, minor and trace elements in solid samples. However, its application for the analysis of liquid samples has been limited due to technical difficulties and high detection limits for most elements (in the mg L^{-1} range) which are not satisfactory for most environmental requirements [2–4]. Therefore, in many studies related to the analysis of liquid samples by XRF techniques, a preconcentration procedure is carried out before the analysis [5]. Taking into account that XRF operates best on solid samples and provides optimal sensitivity and accuracy for thin homogeneous targets, preconcentration procedures leading to solid thin targets are ideal for XRF [6].

We have previously demonstrated the usefulness of laboratory-made selective membranes (activated thin layers) containing the

anion-exchanger Aliquat 336 or the use of commercial solid-phase extraction disks to preconcentrate metals in liquid samples before XRF analysis [7–10].

For the present report, we take advantage of the multielemental capability of the XRF technique and have developed a preconcentration method for the determination of trace amounts of V, Cr, Mn, Fe, Co, Ni, Cu, Zn, Ga, Se, Pb and Cd in environmental liquid samples prior to XRF analysis. The proposed preconcentration procedure consists of a solid-phase extraction using carbon nanotubes (CNTs) as solid sorbents. CNTs are relatively new adsorbents that have advantages compared to other sorbents commonly used for preconcentration purposes (i.e. activated carbon): first, CNTs have a well-defined structure at the atomic scale, making it possible to achieve more reproducible results; second, due to the large surface area and small structures, CNTs have an excellent absorption capacity for organic compounds and heavy metal ions [11,12]. Previous results have demonstrated that better preconcentration rates can be obtained when using oxidized CNTs compared to raw CNTs, due to the introduction of carboxyl and hydroxyl groups in the CNTs surface [13,14]. In this study, we have evaluated the benefits and limitations of different XRF spectrometers for determination of the aforementioned elements loaded in oxidized CNTs. We examined the use of two benchtop energy dispersive X-ray fluorescence (EDXRF) spectrometers with different geometries (2D and 3D geometries) and a large-scale wavelength

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dispersive X-ray fluorescence (WDXRF) instrument. Recent technological advances have led to the availability of benchtop and portable XRF systems that offer extreme simplicity of operation in a low-cost compact design (no cooling media or gas consumption are required for operation), but they also provide limited sensitivity compared with high-scale instrumentation [15].

2. Experimental

2.1. Reagents, solutions and samples

Stock solutions of 1 mg mL⁻¹ of V(V), Cr(III), Mn(II), Fe(III), Co(II), Ni(II), Cu(II), Zn(II), Ga(III), Se(IV), Cd(II) and Pb(II), nitric acid (65% Suprapur[®]) and ammonium hydroxide solution (65% Suprapur[®]) were purchased from Merck (Darmstadt, Germany). Multi-walled CNTs (MWCNTs) were acquired from Sigma Aldrich (Seinheim, Germany). The pH of the analyzed solutions was adjusted with 0.1 mol L⁻¹ HNO₃ and 0.1 mol L⁻¹ NH₃. Multielemental standard solutions containing the aforementioned elements were prepared from the stock solutions. All reagents and solutions were dissolved and diluted with high purity water obtained from a Milli-Q Plus system (Millipore).

River water samples were collected from an industrial area of Poland. The samples were filtered through membrane filters (pore size 0.45 µm, Millipore) and acidified with nitric acid before being analyzed.

2.2. Preconcentration procedure using carbon nanotubes

Specific details for the preconcentration procedure using carbon nanotubes can be found elsewhere [13]. In brief: 100 µL of the target multielemental solution containing V(V), Cr(III), Mn(II), Fe(III), Co(II), Ni(II), Cu(II), Zn(II), Ga(III), Se(IV), Cd(II) and Pb(II) and 200 µL of 5 mg L⁻¹ of MWCNTs were added to 100 mL of water. The pH of the solution was adjusted to 9. Next, the mixture was stirred with a magnetic stirrer for 5 min. After that, the sample was filtered and the MWCNTs with adsorbed elements were collected onto the Whatman filter. The loaded filter was dried under an IR heater and protected using a 0.5 mL of 0.5% (m/v) solution of polystyrene in carbon tetrachloride. Loaded filters were placed between two 6.0 µm-thick Mylar X-ray foils (supplied by Chemplex Industries, Inc., New Cork, USA) mounted in special liquid sample holders that incorporate snap-on rings at the end of the cell for attachments of thin-film supports. Afterwards, samples were sealed in the sample holders of each spectrometer (EDXRF, WDXRF and Polarized-beam EDXRF (P-EDXRF)) for XRF analysis.

As mentioned in the introduction section, better preconcentration rates can be obtained when using oxidized CNTs in comparison with raw ones. The MWCNTs were oxidized using HNO₃ [16].

2.3. Instrumentation

We tested the capabilities of the following three differently configured XRF spectrometers for analysis of the metal-loaded filters: (i) EDXRF benchtop system, (ii) WDXRF instrument and (iii) P-EDXRF benchtop system.

2.3.1. Energy dispersive X-ray fluorescence system (EDXRF)

A touch-control S2 RANGER EDXRF system (Bruker AXS, GmbH, Germany) with a Pd X-ray tube (max. power of 50 W) and a XFLASH™ Silicon Drift Detector (SDD) with a resolution <129 eV at Mn-K_α was used. The instrument is also equipped with nine primary filters that can be selected to improve measuring conditions for elements of interest. Detailed information about specific features of the S2 RANGER spectrometer can be found elsewhere [17].

2.3.2. Wavelength dispersive X-ray fluorescence system (WDXRF)

A commercial WDXRF Rigaku ZSX Primus wavelength dispersive X-ray spectrometer was used. The system is equipped with a 3 kW

Rh-target X-ray tube, ten analyzer crystals, a sealed proportional counter for light element detection and a scintillation counter for heavy elements. Using this equipment, it is also possible to conduct the analysis in a helium atmosphere or vacuum to avoid signal loss by air absorption. Additional information can be found in Ref. [18].

2.3.3. Polarized energy dispersive X-ray fluorescence instrument (P-EDXRF)

Finally, we tested a SPECTRO XEPOS P-EDXRF spectrometer (SPECTRO Analytical Instruments GmbH). This system uses a 50 W Pd end-window X-ray tube and offers many different excitation conditions by using up to 8 polarization and secondary targets. It is equipped with an SDD with a resolution <155 eV at Mn-K_α. Additional information can be found elsewhere [19].

2.3.4. EDXRF with a small spot X-ray beam

In order to study the spatial distribution (homogeneity) of the metals pre-concentrated in the CNTs, a commercial EDXRF system (XDV-SD model, Helmut Fischer GmbH, Sindelfingen, Germany) equipped with a small spot X-ray beam (0.1, 0.3, 1.0 and 3.0 mm) was employed. The main features of this equipment are the use of a low-power tungsten X-ray tube operating at a maximum power of 50 W (operating at fixed voltage of 10, 30 and 50 kV and within a range of 0.1 to 1 mA) and a Si-PIN semiconductor detector (Peltier cooling at -50 °C) with an energy resolution of 180 eV at 5.89 keV (Mn K_α line). The use of an XYZ programmable motorized stage enables fully automatic measurements. The instrument is controlled by the WinFTM[®] – V.6.20 software, which is also used for both spectral acquisition and spectral data treatment. This software is based on the principles detailed in the Roessiger & Nensel work [20].

3. Results and discussion

3.1. Preconcentration procedure using carbon nanotubes and XRF analysis

In a former study, the preconcentration procedure using CNTs was optimized for various analytical parameters including the pH and volume of the aqueous sample, the amount of CNTs and the extraction time in order to achieve the best performance for multi-element preconcentration [13]. In the present contribution, parameters affecting the analysis of the metal loaded CNTs on the filters by means of XRF instrumentation were evaluated.

As detailed in Section 2.2, after the preconcentration procedure, the aqueous sample was filtrated and CNTs with adsorbed elements were collected onto a Whatman filter. It was found that the area of the loaded CNTs on the filter was a critical parameter to be taken into consideration when performing the subsequent XRF analysis. If the area of the loaded CNTs on the filter is too large, only a small fraction of the extracted elements is excited and, in consequence, a low intensity of fluorescence radiation is observed. For this reason, in order to work under conditions of higher sensitivity, we used a vacuum filter assembly with a diameter of 30 mm instead of the most commonly used size of 47 mm. Another important issue for the later XRF analysis, is the placement of the loaded filter on the spectrometer sample holder. In order to avoid any radiation from the edge of the sample holder aperture of the spectrometer, loaded filters were placed between two 6.0 µm-thick Mylar X-ray mounted in special liquid sample holders that incorporate snap-on rings at the end of the cell for attachments of thin-film supports (see Fig. 1). Afterwards, samples were sealed in the sample holders of each spectrometer for subsequent XRF analysis.

A study to evaluate the spatial distribution (homogeneity) of pre-concentrated elements on the loaded filters was also conducted. For this, a multielemental solution containing 15 µg of each element was pre-concentrated and the obtained loaded filter was analyzed using an EDXRF system equipped with a small spot X-ray beam (see instrumental parameters described in Section 2.3.4). The measurement routine consists of the analysis of a grid of 10 × 10 points distributed

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