Possibilities of Micro X-Ray Fluorescence Spectrometry of Solutions with Preconcentration

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Received November 13, 2012; in final form, October 22, 2013

Abstract—Results of investigations in energy-dispersive X-ray fluorescence analysis aimed at the development of a high-sensitivity method of microanalysis of solutions are presented. A combined scheme of analysis of one drop of solution of the volume several microliters is proposed and tested. The scheme includes a new preconcentration method based on the drop evaporation in the presence of a micrograin of a hydrophilic adsorbent followed by the microanalysis of the solid phase on the portable device with a polycapillary lens with a focal spot of 10 µm designed at the Institute of Physical Optics. Analytically meaningful X-ray fluorescence spectra were obtained using DETATA (grain diameter about 100 µm) and SAC8 (50 µm) adsorbents and individual drops of model solutions containing Mn, Fe, Co, Ni, Cu, and Zn (0.2 mg/L and higher) and analytical characteristics of the proposed approach are demonstrated.

Keywords: X-ray fluorescence analysis, sample preparation, preconcentration, polycapillary optics

DOI: 10.1134/S1061934814060033

Combined schemes of analysis of solutions, including adsorption preconcentration of trace elements and their determination in the adsorbent phase or in a liquid concentrate obtained by subsequent desorption are widely used in present-day analytical chemistry to reduce the limits of detection for trace elements [1–3]. Such analytical schemes involve various instrumental methods, in particular, energy-dispersive X-ray fluorescence analysis (EDXRF), suitable for the analysis of solids. This method allows the simultaneous determination of a great number of elements. Contemporary instruments for EDXRF are quite simple and available; however among their drawbacks is low sensitivity. The limits of detection for elements with medium atomic numbers for routine devices are no lower than several dozen ppm (mg/L). The method ideally fits into combined schemes of analysis by the sets of its positive and negative characteristics.

Previously the researchers of the Institute of Physical Optics and the Vernadsky Institute of Geochemistry and Analytical Chemistry of the Russian Academy of Sciences have developed highly sensitive experimental instruments for EDXRF with replaceable reusable concentration cartridges designed a layer of micrograins of one or another adsorbent irradiated by primary X-ray beam [3–7]. The substrates for micrograins were polycapillary structures consisting of hundred thousands of identical microchannels. A new version of sorption–X-ray fluorescence method was proposed for determining metals in solutions based on the use of the laws adsorption kinetics and requiring no quantitative extraction of the analytes from the test solution [3, 8]. On an example of determining 0.3–2.0 mg/L Mn, Fe, Ni, Cu, and Zn in tap water the analytical characteristics of the proposed approach were demonstrated along with the possibilities of reducing the limits of detection for metals by two orders of magnitude. The possibility of the further decrease of the limits of detection for metals to below 0.1 mg/L was shown experimentally using X-ray schemes of the creation of a quasiparallel X-ray beam [6, 8].

In spite of the advantages of proposed approach, certain restrictions remain for the application of EDXRF; these are associated with the long duration of analysis (1–2 h) and the necessity of using large volumes of tests solutions (dozens milliliters and more), especially at low analyte concentrations. Preliminary investigations have shown that the sophistication of the sorption–X-ray fluorescence method, in particular, the reduction of the volumes of analyzed samples and even the change to the microanalysis of solutions, the further reduction of the limits of detection and the duration of analysis are associated with the possibility of focusing of the irradiating X-ray beam [8, 9]. A similar problem for direct X-ray fluorescence microanalysis was solved using systems of polycapillary X-ray optics (polycapillary lenses) proposed by one of authors of this paper [10–12].
The aim of this work was an experimental study of the key possibility of the microanalysis of solutions in a combined scheme utilizing EDXRF with X-ray optics.

**EXPERIMENTAL**

**Instruments.** The experiments were conducted on an MX-10 microX-ray fluorescence spectrometer utilizing an X-ray scheme, designed at the Institute of Physical Optics and assembled by one of the authors of this work (Fig. 1a). In the instrument we used polycapillary lens U255d8f4-3-20100603 with a focal spot of 10 μm, also produced in the Institute of Physical Optics. The other main accessories were a small-sized monoblock unit containing an LLF X-ray tube with a copper anode of the power up to 5 W combined with a high-voltage power unit XRS-5/35 (Yunisantis Open Company, Russia); a semiconductor Si-Pin detector with a resolution of 135 eV and a Colibri pulse analyzer (Green Star SE, Russia); and a portable digital DinoLite USB microscope with a maximum magnification of 92X (ANMO Electronics, Taiwan).

**Model solutions and adsorbents.** We used model solutions of NaCl (0.25 g/L) in deionized water, each containing equal amounts of trace components (Fe, Mn, Co, Ni, Cu, and Zn). Different model solutions differed by the concentrations of trace components, which were varied from 0.2 to 2 mg/L for each metal.

Preconcentration was conducted using samples DETATA adsorbent with diethylenetriaminetetraacetic groups prepared as spherical micrograins by G.I. Tsizin with coauthors at the Division of Analytical Chemistry of Moscow State University [1]. Before use we performed sedimentation separation in a conc. NaCl solution and also the sieve analysis of the adsorbent by its granulometric composition. We also used a SAC 8 sulfopoliostyrene cation exchanger (8% of cross-linking agent divinylbenzene) shaped as microspheres (size 50 μm) from KhromResurs Open Company, Russia.

**Experimental procedure.** A sample holder made of fluoroplastic as a sectional hollow cylinder (H = 20 mm, D = 30 mm) with an aperture at one end face (d = 10 mm) onto which a mylar film (X-ray transparent polyethylene terephthalate film with low water affinity) 6 μm thick was drawn on during assembly as shown in Fig. 1b was put onto the object stage of the spectrometer. An adsorbent micrograin was placed on the film near the aperture at the end face of the holder, fixed at the microscope focus; all manipulations were observed on a computer monitor. The focus of the X-ray lens was adjusted to the adsorbent grain using X-Y-Z movements so that all grain remained within the beam of primary X-ray radiation. These manipulations took no more than 1–2 min. The fluorescence spectrum of the initial adsorbent (blank experiment) was recorded under the following conditions: voltage on the anode 30 kV, current 100 μA, time of accumulation from 100 to 300 s. A micrograin was covered with a drop of test solution 1 or 2 μL in volume using an analytical microsyringe as shown in Fig. 2. In the work with model solutions the drop was allowed to dry within 10–15 min, then the fluorescence spectrum...