Spectrochimica Acta Part B 99 (2014) 59–66

Contents lists available at ScienceDirect

Spectrochimica Acta Part B

journal homepage: www.elsevier.com/locate/sab

Applicability of direct total reflection X-ray fluorescence spectrometry for multielement analysis of geological and environmental objects[☆]

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ARTICLE INFO

Article history:
Received 16 November 2013
Accepted 18 May 2014
Available online 22 June 2014

Keywords:
TXRF
Natural water
Rock
Mineral
Suspension

ABSTRACT

The research aim is to demonstrate our experience in the applicability of TXRF analysis of various geological and environmental objects using minimal sample treatment. The study was focused on the evaluation of different factors affecting the TXRF results obtained for solid and liquid samples such as rock, mineral, ore, and natural water. Powdered geological samples were prepared as suspensions. Natural water samples were analyzed directly or after dilution. Testing various experimental parameters, e.g. sample amount, type of dispersant, and others was performed. For chosen conditions of the sample preparation procedure analytical figures of merit were estimated. Presented analytical results display the possibilities of TXRF applications in geological and environmental fields.

1. Introduction

The precise determination of major and trace elements in geological and environmental objects is necessary for petrogenetic, geochemical, and environmental researches [1]. For instance, studying the pattern of trace and rare earth element (REE) distributions in rocks and minerals enables us to determine the conditions of rock forming and concern to exogenic or endogenic types of rocks. The research of large ion lithophile elements such as Pb and U in accessory apatite, which occurs in magmatic rocks, can be used for the rock dating in the case of their large contents. The Rb, Sr, Cs, Ba, and Pb determination in the K-feldspars is very important for the evaluation of rare-metal ore contents in the pegmatites [2]. The data on the water elemental composition give the possibility to classify different types of natural waters to get the information about way of water genesis. It can be used for environmental monitoring and testing the water quality for potability and therapeutic application [3].

Commonly, the elemental composition of various geological and ecological objects is investigated by X-ray fluorescence (XRF) and inductively coupled plasma mass spectrometry (ICP-MS) [4–6]. For conventional XRF analysis, reasonably large sample amount of powder, set of calibration standards, and matrix corrections are usually required. In most of studies related to the analysis of liquid samples by XRF techniques, a preconcentration procedure is needed before the analysis [7]. ICP-MS is well-established analytical tool with good figures of merit for trace and ultra-trace element determinations in various sample types. This method requires the use of expensive equipment and complicated sample preparation procedures such as acid digestion or lithium metaborate fusion.

Total reflection X-ray fluorescence (TXRF) spectrometry is proposed as suitable multielement and microanalytical method, which has benefits such as minute sample amounts, low detection limits, and the capability of simultaneous multielement determination [8]. Analysis schemes and sample preparation procedures, described in the literature, are various and highly dependent on the type of object analyzed by TXRF. Traditionally, TXRF spectrometry is applied for the analysis of the liquid samples. The review of the literature in the last decades has shown that dozens of publications covering water analysis are available. Different types of natural waters, e.g. fresh [9], mineral [10], and river [11] can be analyzed using TXRF directly or after filtration. For sea [12] and waste [13] water direct TXRF is difficult because of high contents of salt matrix and organic substances, so before TXRF the preconcentration or the dilution procedures are recommended.

In recent years there are a sufficient number of the TXRF publications dedicated to the study of geological objects such as rocks, river sediments, soils, and minerals [14–21]. Therefore, most of these researches were performed using a digestion for the samples analyzed [14–18]. In works in Refs. [19–21] the preparation of the powder samples as suspensions is suggested.

The main goal of our research is to study the possibility of direct TXRF to simplify sample preparation procedure for different types of natural materials, which are commonly used in environmental and geochemical studies.

[☆] Selected paper from the 15th International Conference on Total Reflection X-Ray Fluorescence Analysis and Related Methods, and the 49th Annual Conference on X-Ray Chemical Analysis (TXRF2013), Osaka, Japan, 23-27 Sept. 2013.

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http://dx.doi.org/10.1016/j.sab.2014.05.013

2. Experimental

2.1. Instrumentation

The measurements were performed using a benchtop S2 PICOFOX™ TXRF-spectrometer (Bruker AXS Microanalysis GmbH, Germany). The TXRF-spectrometer is equipped with a metal-ceramic X-ray tube with a Mo-anode and air cooling, a planar multilayer monochromator (Ni/C), and XFlash® Si drift detector (SDD) with an area of 30 mm^2 and <150 eV resolution for the Mn K_α-line. Detailed information about the S2 PICOFOX™ instrument can be found elsewhere [22]. The measurements were conducted at 50 kV operating voltage and 750 μA current. The measurement time was 1000 s per sample. The treatment of the X-ray spectra and the account for separate fluorescence peak overlaps were performed using the software SPECTRA 5.3 [23].

High resolution instrument ELEMENT-2 (Finnigan MAT, Germany) was used for the ICP-MS measurements. The K-feldspar samples were analyzed by flame photometry (FP) method using a DFS-12 diffraction spectrometer (Russia) with a propane air flame as it was described in [2].

2.2. Reagents and materials

Gallium inductively coupled plasma (ICP) standard solution with the concentration of 1000 mg/l, selenium ICP standard solution with the concentration of 1000 mg/l, ICP multi-element standard solution XVI with the concentration of 100 mg/l of Sb, As, Be, Cd, Ca, Cr, Co, Cu, Fe, Pb, Li, Mg, Mn, Ni, Se, Sr, Tl, Ti, V, and Zn was purchased from CertiPUR®, Merck (Germany).

High purity water deionized with Mill-Q water purification system (Millipore) and non-ionic detergent Triton X-100 (reagent grade, Amresco) were used for the dilution of samples analyzed. Chemically pure reagents of sodium chloride and magnesium sulfate used for preparing salt solution were produced by Reachem GmbH (Russia) [24].

Quartz glass discs with a 30 mm diameter and a thickness of 3 mm ± 0.1 mm were applied as TXRF sample carriers. Sample carriers were previously siliconized by 10 μl of a silicon solution in isopropanol (Serva™, Germany) to avoid spreading of the analyzed samples on the surface of the carriers.

2.3. Samples

To perform our study we selected different types of geological and environmental samples.

2.3.1. Geological samples

Geological samples of K-feldspars, apatites, rocks, and manganese ores, which have different chemical composition and a bulk density, were carefully studied. The Certified Reference Materials (CRMs) and the Reference Materials (RMs) of granites, granodiorites, rhyolite, K-feldspars, basalt, carbonatite, and manganese ores compositions were used. These CRMs were produced and certified by the Central Geological Laboratory of Mongolia [25] (granites OShBO and MGT-1), and RMs were produced by the United States Geological Survey [26] (USGS) (granites G-2, GA, rhyolite RGM-1, basalt BHVO-2, carbonatite COQ-1), the Geological Survey of Japan [27] (granodiorites JG-1, JG-2 and K-feldspars JF-1, JF-2), Bronnitskaya geological–geochemical expedition at the Geological Ministry of USSR [28] (apatite concentrate AK 2462-82, apatite ore 5750-86), and Centergeolanalit GmbH, Kazakhstan [29] (oxydic manganese ores 5406-90 and 5404-90).

2.3.2. Natural water

The samples of natural waters of various contents of total dissolved solids (TDS) such as fresh, mineral, ground water, and brines have been selected for the experiments. The TDS was determined by evaporating a known volume of water and drying at 110 °C to a constant weight. For testing the accuracy, the samples of brine, mineral, and fresh water were analyzed by standard methods of “wet” chemistry such as argentometry (Cl), trilonometry (Ca), gravimetry (SO_4^{2-}), iodometry (Br), and flame emission spectrometry (K, Rb, and Sr) in the laboratory of hydrology at the Institute of the Earth's Crust, SB RAS. The ground water samples were analyzed by ICP-MS at the Institute of Geochemistry, SB RAS.

2.4. Sample preparation method

2.4.1. Preparation of solid samples

Suspensions of the rock CRMs and RMs, the K-feldspar, apatite, and manganese ore samples were prepared. The rock CRMs and RMs are powders with a particle size as low as 63 μm. The particle sizes of the geological sample powders were studied using the electron probe X-ray microanalyzer Superprobe JXA-8200 (JEOL, Japan).

Rock sample powder weighing about 10–100 mg was suspended in 2.5 ml of aqueous 1% Triton X-100 solution. The volume of 100 μl of the Se standard solution with the concentration of 100 ppm was added to the prepared suspension as the internal standard. An aliquot of 10 μl was transferred on a siliconized quartz glass sample carrier and dried on a heating plate. After drying, a thin hydrophobic film remains on the surface of the sample carriers. The amount of dry residue on the sample carrier was 40–400 μg.

The oxydic manganese ore RM 5406-90 powder was prepared as a suspension. Aqueous 1% Triton X-100 solution was chosen as a dispersant for the ore suspension preparation. Then 10 ml of the dispersant was mixed with 10, 20, 50, and 100 mg of the sample powder. The Se standard solution with the concentration of 1 g/l was added to the suspension, so that the final concentration of Se in the dry residue would be 1000 ppm. An aliquot of 10 μl was dropped on a siliconized sample carrier and dried on the heating plate.

For all solid samples, three replicates were prepared and each one was measured twice in each experiment.

2.4.2. Preparation of liquid samples

Samples of sodium-chloride brines (TDS = 220–300 g/l) were diluted with the 1% solution of Triton X-100 varying the degree of the dilution from 3 to 1000. Fresh (TDS = 0.2–0.3 g/l) and ground (0.4–0.5 g/l) waters were analyzed directly after acidification with 60% distilled HNO_3. For analysis of mineral water (TDS = 3 g/l), two samples (original and acidified) were analyzed after the dilution 2 times. In all cases an appropriate amount of Ga solution (the Ga concentration depended on the type of water) was added to the sample as the internal standard. The resulting solution was homogenized and an aliquot of 10 μl was deposited on the siliconized quartz glass carrier and dried. For each experiment three replicates were prepared and each one was measured twice.

In order to study the effect of hydrophobization on the TXRF results, 10 μl of the ground water sample was dropped onto the quartz carriers with and without pre-treatment by the silicone solution. In each case ten independent dry residues were prepared and measured twice.

To evaluate the effect of salt contents on the detection limits (DLs) of trace elements, solutions containing 32,000, 3200, 320, and 32 mg/l of mineral substances were prepared by mixing NaCl and $MgSO_4$ salts. The multi-element standard solution XVI was added to the prepared salt solutions, so that the resulting concentrations of analytes were 1 mg/l.

3. Results and discussion

3.1. TXRF analysis of solid samples

3.1.1. Sample preparation approaches

In our research the following approaches for the slurry sample preparation were applied.