Talanta 160 (2016) 375–380

Contents lists available at ScienceDirect

Talanta

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

Analytical approaches for determination of bromine in sediment core samples by X-ray fluorescence spectrometry

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ARTICLE INFO

Article history:
Received 26 April 2016
Received in revised form
20 July 2016
Accepted 24 July 2016
Available online 25 July 2016

Keywords:
X-ray fluorescence analysis
WDXRF
TXRF
Sediments
Bromine
Paleoclimate

ABSTRACT

Bromine has been recognized as a valuable indicator for paleoclimatic studies. Wavelength dispersive X-ray fluorescence (WDXRF) and total reflection X-ray fluorescence (TXRF) methods were applied to study the bromine distributions in lake sediment cores. Conventional WDXRF technique usually requires relatively large mass of a sediment sample and a set of calibration samples. Some analytical approaches were developed to apply WDXRF to small sediment core samples in the absence of adequate calibration samples with a known Br content. The mass of a sample to be analyzed was reduced up to 200–300 mg and the internal standard method with correction using fundamental parameters was developed for Br quantification. TXRF technique based on the direct analysis of a solid suspension using 20 mg of sediment sample by internal standard method was additionally tested. The accuracy of the WDXRF and TXRF techniques was assessed by the comparative analysis of reference materials of sediments, soil and biological samples. In general, good agreement was achieved between the reference values and the measured values. The detection limits of Br were 1 mg/kg and 0.4 mg/kg for WDXRF and TXRF respectively. The results of the Br determination obtained with different XRF techniques were comparable to each other and used for paleoclimatic reconstructions.

1. Introduction

Data about the element distributions in lake sediments are widely used to reconstruct changes in the environment and climate. One of the geochemical indicators of the paleoclimatic changes is bromine whose concentration is increased in the warm periods and correlated with the content of organic matter in sediments reflecting the biological productivity of the lake [1–4].

For determining Br due to volatility of its compounds it is preferable to use non-destructive analytical methods, one of them is X-ray fluorescence (XRF) spectrometry [5,6]. Different variants of XRF spectrometers can be used for studying composition of sediments. In order to rapidly assess elemental variations in unprocessed wet sediments, X-ray fluorescence core scanner provides a semi-quantitative estimate of Br (total counts or counts per second). However reliable climate high-resolution reconstructions require absolute concentrations of elements [7]. Phedorin and Goldberg [7] suggested a method for quantification of elements in natural wet sediments (cores) from their scan measurements using XRF with synchrotron radiation (SR-XRF). SR-XRF also can be applied for sensitive multielement determinations from 30 to 40 mg of drying, powdering sediment core fragments pressed into tablets. Despite the obvious advantages of SR-XRF, the use of synchrotron radiation is still not considered a routine available method.

Conventional wavelength dispersive XRF (WDXRF) or energy dispersive XRF (EDXRF) spectrometers have been widely applied to the determination of bromine in various environmental and geological investigations. Standard sample preparation procedures for XRF usually require several grams of sample. For instance, to determine the bromine in sediments, a sample weighing at least 1 g (e.g., 1 g [8], 2 g [9], 4 g [10], 5 g [11] 7 g [12]) is pressed into a tablet with a diameter of 25–40 mm. Large sample amount (more than 500 mg) limits application of XRF to high-resolution records in paleoclimatic studies. Another problem, which makes the use of XRF difficult, is the need for certified reference materials (CRMs) of sedimentary rocks to apply traditional calibration curve method. However the recommended or certified values for bromine are available only for a small number of CRMs [10,13]. To overcome this, the labor-intensive standard addition method or synthetic calibration samples have been applied for Br determination [5,6,10,12].

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http://dx.doi.org/10.1016/j.talanta.2016.07.059
0039-9140/

Total reflection X-ray fluorescence (TXRF) has a good potential for solving paleoclimatic problems because small sample amounts needed (mg range) and quantitative analysis is performed using an internal standard method. To our knowledge, relative few papers exist on direct quantification of Br in geological samples by TXRF, e.g. apatites [14], carbonatites, and silicate rocks [15], alkaline rocks [16], tills [17], soils [18], and there are no publications about Br determination in sediment cores.

In this work, some analytical approaches were developed to obtain information on the distribution of bromine in lake sediment cores by WDXRF technique in the absence of adequate calibration samples with a known Br content. TXRF was additionally tested and the results, obtained by different X-ray fluorescence methods, were compared with each other.

2. Experimental

2.1. Instrumentation, reagents and materials

2.1.1. WDXRF

A S8 Tiger wavelength-dispersive X-ray fluorescence spectrometer (Bruker AXS, Germany) equipped with a Rh anode X-ray tube and 4 kW excitation power was used. Measurements of the characteristic Br Kα line were performed under vacuum at 50 kV and 50 mA tube setting and using 8 mm mask, LiF(200) crystal, 0.46° collimator, and scintillation counter. The adjusted peak position of Br $K\alpha_1$ was set to a 2θ value of 29.97°, the background positions were set at 29.42° and 30.78°.

Samples were pressed using a semi-automatic hydraulic HERZOG HTP-40 press (Germany) in a 40 mm press tool. Analytical grade crystalline boric acid was used as a backing and rim material. A sample holder fitted with stainless steel masks having openings of 8 mm in diameter was applied for XRF measurements.

2.1.2. TXRF

The measurements by TXRF were performed with a benchtop spectrometer "S2 PICOFOX" (Bruker Nano GmbH), equipped with the micro-focus X-ray tube (Mo-anode, 50 kV voltage, 750 μA current), the multilayer monochromator (Ni/C), the 30 mm^2 XFlash® SDD with an energy resolution of about 150 eV at MnKα-line. The treatment of the X-ray spectra and the calculations were performed using the software SPECTRA 5.3 with deconvolution based on a Bayesian inference (Super Bayes).

Germanium inductively coupled plasma standard solution with the concentration of 1000 mg/l 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. Quartz glass discs with a 30 mm diameter and a thickness of 3 ± 0.1 mm were applied as TXRF sample carriers.

2.2. Sample preparation and measurement

2.2.1. Samples

Sediment cores were collected from Lake Baikal and Lake Khara-Nur (Russia). The core of the Baikal bottom sediments was collected on the Posolsk Bank (shoal) at the southern termination of the Selenga-Buguldeika saddle by gravitation pipe from board the research vessel "Vereschagin". Thickness of sediments reaches 305 cm and core diameter is 110 mm. The bottom sediments core consists of biogenic-terrigenous mud with a high content of diatomic algae residues (up to 25–27%) to a depth of 90 cm and glacial-lake clays with a low content of diatoms (~3%). The age of the whole profile is approximately 25 ± 5 thousand years.

The core of the bottom sediments of Khara-Nur Lake (Eastern Sayan Mountains) was collected by gravity corer UWITEC from the boat [19]. Thickness of sediments reaches 130 cm and core diameter is 53 mm. A lacustrine thickness of the lake sediments involves biogenic-terrigenous mud with high concentrations of diatoms (both cyclic and peanut forms), where the proportion of terrigenous and biogenic components is almost equal. The age of the core is limited to middle Holocene (about 5500 years). Results of preliminary studies of this core, including the distribution biogenic opal ($SiO_{2\ bio}$) and chemical index of alteration (CIA), have been published earlier [19].

The both cores in depth were divided into individual horizons with an interval 0.5–1 cm. Each core fragment was dried at 50–60 °C and manually homogenized using an agate pestle and a mortar. Sediment aliquots of approximately 0.5–1 g were selected for X-ray fluorescence investigations from bottom to top of the core (25 subsamples from the lake Baikal core and 200 subsamples from the lake Khara-Nur core).

Gallardo et al. [18] demonstrated that the particle size can affect the Br determination by TXRF and the particle size should be lower that 63 μm to obtain quality analytical results. Granule size and distribution in the investigated sediment powders were examined with laser diffraction analysis by Laser Particle Sizer "ANALYSETTE 22" Compact (Fritsch GmbH). According to the measurements, the powder particles were less than 50 μm in diameter which is acceptable for WDXRF [20] and TXRF [18] techniques.

2.2.2. Standard reference materials

CRMs of Baikal bottom silts BIL-1,2 (CRMs 7126-94, 7176-95), silts SGH-1,3,5 (CRMs 3131-85, 3132-85, 3133-85), and sediments SGHM-1,2,3,4 (CRMs 3483-86, 3484-86, 3485-86, 3486-86), leaves of birch LB-1 (CRM 8923-2007), Canadian pondweed EK-1 (CRM 8921-2007), and Lake Baikal perch tissues BOk-2 (CRM 9055-2008) were produced by Institute of Geochemistry SB RAS [21]. MAG-1 marine sediment and GXR-5 soil were produced by USGS and USGS-AEG [22]. The data for CH-1 marine sediment were obtained by the international proficiency testing program for analytical geochemistry laboratories GeoPT10 [23].

2.2.3. Sample treatment procedure for WDXRF

A S8 Tiger spectrometer offers the potential to decrease the quantity of material to be analyzed by using a mask to cut out the irradiated surface from 34 mm to 8 mm. It allows modifying the preparation procedure consisting in weighing 1 g of powder sample and pressing into cylindrical pellets of 40 mm in diameter on the boric acid backing [24]. For our study 200–300 mg of a sample (depending on its poured density) was transferred in a steel ring of 10 mm in inner diameter placed in the center of a 40 mm press mould, and then a ring was removed and a sample was covered by 9 g of boric acid and pressed at a pelletizing pressure of 10 t. As a result, a specimen of 10 mm in diameter on the boric acid backing of 40 mm in diameter was formed (Fig. 1).

The infinite thickness required to absorb 99% of radiation and calculated for the sediment composition (SiO_2 – 64, Al_2O_3 – 15, Fe_2O_3 – 6, CaO – 7, MgO – 3, Na_2O – 3, K_2O – 2 wt%) was equal to 60 μm which means 130 mg for specimen with 10 mm of diameter, then under the chosen sample preparation conditions the specimen satisfies the infinite thickness criteria.

2.2.4. Sample treatment procedure for TXRF

Solid suspensions using a non-ionic surfactant Triton X-100 as a dispersing agent were prepared from powdered samples. In our previous work [25] it was shown that mass of the suspended sample more than 50 mg can lead to the absorption effects. According to the literature, the best results of Br determination in soil [18] and organic fertilizers [26] were obtained by suspending

Please cite this article as: G.V. Pashkova, et al., Talanta (2016), http://dx.doi.org/10.1016/j.talanta.2016.07.059