Quantitative approaches to the determination of elements in lake sediments by total reflection X-ray fluorescence

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ABSTRACT

Element distribution data in lake sediments are widely used to study environmental and climate change over geological time scales. Total reflection X-ray fluorescence (TXRF) seems to be well suited for fast multi-elemental analysis of small quantities of subsamples obtained by cutting a sediment core at different intervals. The TXRF technique based on the direct analysis of a suspension prepared by mixing 20 mg of powdered sample and 2 mL of an aqueous 1% Triton X-100 solution was applied to the various reference materials of sedimentary rocks and samples of lake sediments to determine Al, K, Ca, Ti, V, Cr, Mn, Fe, Ni, Cu, Zn, Rb, Sr, and Ba contents. It was shown that the element internal standard, as well the Compton scattered peak, can be used to compensate the error associated with the sample deposition process. Different quantitative approaches have been proposed and evaluated using the reference materials of the sedimentary rocks: (i) internal standardization, (ii) external calibration with correction by means of adding an internal standard, (iii) external calibration with the 'fluorescent-to-Compton' correction. It was shown that the external calibrations can compensate systematic overestimation or underestimation of the TXRF results obtained using the internal standard method, especially for Al, K, V, Cr, Zn, Rb, and Ba. The TXRF results for Ca, Ti, Mn, Fe, Ni, Cu, and Sr weakly depend on the quantitative procedure.

1. Introduction

One of the most popular geological applications of X-ray fluorescence (XRF) spectrometry is the analysis of lake and ocean core sediments to study environmental and climate change over geological time scales [1]. Absolute changes in the element concentration with the depth of the core are obtained by means of analyzing dry, powdered, homogenized sediment fragments [2,3]. It is important to emphasize that complex high-resolution studies require analyzing large number of discrete samples, whose quantities are often limited (< 500 mg) [3,4]. From this point of view, total reflection X-ray fluorescence (TXRF) seems to be well suited for multi-elemental analysis of small quantities of subsamples obtained by cutting the sediment core at different intervals.

Reliable reconstructions of the environmental changes using element profiles are only possible if the errors owing to the sample preparation and quantification procedures are minimized. As it was shown in previous studies [5–15], the preparation of solid samples as slurries before TXRF is a good alternative to digestion procedures. Commonly, 10–50 mg of a powdered sample is applied to preparing suspension. Analytical approaches based on the direct analysis of a solid suspension by TXRF and the quantification by the internal standard method is carefully described in the literature for various types of complex samples. However, the reliable quantification of some elements is still problematic due to the absorption effects, especially in low-Z region of the TXRF spectra [11,12,14], as well as the instability of solid suspensions [14]. Moreover, particle size, mineralogy and morphology effects as well as inaccurate deconvolution of the TXRF spectra due to the overlaps between analyte and pile-up peaks, can lead to either under- or overestimation of the true concentration of the analyte [5,8,13,15]. To overcome the difficulties associated with the quantitative analysis of slurries, some procedures applied, for example, external calibration for K and Ca in food [11], applying a correction factor in the analysis of human placenta samples [12] and building materials [14], recalibration of spectrometer using real samples with known element concentrations [5].

TXRF advantages such as the possibility of fast elemental analysis of small sample amounts prepared as slurries let us to apply this technique to the determination of Br in the sediment core [4]. The goal of the present research is to minimize the error in the quantification of the expanded set of the elements of interest (Al, K, Ca, Ti, V, Cr, Mn, Fe, Ni, Cu, Zn, Rb, Sr, and Ba). Different quantitative approaches have been proposed and evaluated using the reference materials of the sediments: (I) internal standardization, (II) external calibration with the correction by means of adding an internal standard to the sample, (III) external calibration with the ratio of the fluorescent peak to the Compton scattered peak. The fluorescence-to-Compton ratio has been widely used in the analysis of organic and mineral samples by conventional XRF to compensate matrix effects and variations of the sample mass and density. In the TXRF analysis, the fluorescence-to-Compton ratio was successfully applied to organic samples, e.g. diesel fuel [16], petroleum crude oil [17], blood serum and human brain [18,19], instead of the quantification based on the adding internal standard. To our knowledge, there are no published scientific contributions about the using Compton peak in the quantitative analysis of the sediments by TXRF.

2. Materials and methods

2.1. Instrumentation

The measurements were performed using a benchtop S2 PICOFOX™ TXRF-spectrometer (Bruker Nano GmbH, Germany) equipped with a micro-focus X-ray tube with a Mo-anode and air cooling, a planar multilayer monochromator (Ni/C), and a Si drift detector (SDD) XFlash® with an area of $30\,mm^2$ and 150 eV resolution for the MnKα-line. All 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 calculations were performed using the software SPECTRA 6 with the deconvolution based on a Bayesian inference (Super Bayes). The intensity of the Compton scattered peak was selected around the region of interest (ROI) at 16.9 keV.

2.2. Geological reference materials

We used the certified reference materials of Baikal bottom silts (BIL-1, BIL-2), carbonate, terrigenous and anomalous silts (SGH-1, SGH-3, SGH-5), carbonate, carbonate silicate and aluminosilicate loose sediments (SGHM-1, SGHM-2, SGHM-3, SGHM-4), which were produced and certified by Vinogradov Institute of Geochemistry of Siberian Branch of the Russian Academy of Sciences [20]. The certified reference materials of clays, slits and ooze (SDO-1 (OOPE101), SDO-3 (OOPE401), SDO-8 (OOPE402), SDO-9 (OOPE501)) were produced and certified by the Research Institute of Applied Physics (RIAP) at Irkutsk State University (Russia) [20]. Also for the study, the reference materials such as CH-1 (marine sediment, GeoPT-10), MSAN (ocean floor sediment, GeoPT-15) and SdAR-1 (modified river sediment, GeoPT-31) were provided by the International Association of Geoanalysts [20].

2.3. Samples

Samples in an amount of 50 pieces were divided from the sediment core of Lake Khara-Nur (Eastern Sayan Mountains, Russia) [4,21], dried at 50–60 °C and homogenized using an agate mortar with a pestle. Because only small amount of the sample are analyzed by TXRF, the sample must be homogenous to ensure representative results [5]. Particle size in the studied sediment powders was examined using the diffraction analysis by a Laser Particle Sizer "ANALYSETTE 22" Compact (Fritsch GmbH). According to the measurements, the average particle size is 15–20 μm, which is acceptable for the TXRF technique [10,15].

Table 1
Relative standard deviations (%) of ten replicates prepared from the reference materials SGH-3 (background silt) and SDO-1 (terrigenous clay).

Element	SGH-3			SDO-1		
	I_i	I_i/I_{Ga}	I_i/I_{inc}	I_i	I_i/I_{Ga}	I_i/I_{inc}
Al	16	4.3	4.8	17	3.7	3.6
K	15	3.0	2.7	16	2.4	2.1
Ca	13	5.4	6.1	15	6.5	6.3
Ti	17	6.6	5.5	16	3.1	3.4
V	15	6.1	4.7	16	4.4	4.7
Cr	14	5.3	5.1	16	2.7	2.8
Mn	13	2.9	2.2	16	6.0	6.5
Fe	13	3.4	2.7	15	1.9	2.5
Ni	16	4.8	3.6	16	2.6	2.6
Cu	15	3.8	3.3	15	3.1	3.5
Zn	14	4.2	3.6	16	2.3	2.8
Rb	15	4.8	3.0	19	3.4	2.8
Sr	13	5.8	4.4	15	2.6	2.7
Ba	15	4.7	4.6	17	1.8	2.2

2.4. Sample preparation

The solid suspensions were prepared by weighting 20 mg of the powdered samples and adding 2 mL of a 1% non-ionic surfactant Triton X-100 solution (reagent grade, Amresco) as a dispersing agent [4]. The Ga standard solution with concentration of 100 mg/L was prepared from the Ga stock solution with concentration of 1000 mg/L (CertiPUR®, Merck). A volume of 200 μL of the Ga solution of 100 mg/L was added to the 2 mL of the suspension as the internal standard, so that the final Ga concentration in the dried sample residue would be 1000 ppm. The resulting mixture was thoroughly homogenized and 10 μL of the suspension was pipetted onto a quartz glass carrier and dried at room temperature.

2.5. Quantification by TXRF

The quantitative analysis by TXRF is usually accomplished by the internal standardization based on the adding some element that is not initially present in the sample. In our study, a known amount (C_{Ga}) of the Ga solution was added into each sample since Ga was not detected in the original samples and the Ga concentration in the reference materials is < 10 mg/kg. The concentration of unknown element C_i is calculated using the relation:

$$C_i = \frac{I_i/S_i}{I_{Ga}/S_{Ga}} C_{Ga},$$ (1)

where I is the net intensity; S is the instrumental sensitivity. The manufacturer software SPECTRA 6 contains database of the sensitivity factors (S) calibrated at factory for Kα- and Lα-lines of elements from Al to U. According to the manufacturer's recommendations, the S2 PICOFOX spectrometer does not require any recalibration of the sensitivities.

Two variants of external calibrations using reference materials of the sediments were considered. The first calibration procedure involved the construction of the calibration curves by plotting the ratio of I_i/I_{Ga} against the reference concentrations:

$$C_i = a \cdot I_i/I_{Ga} + b,$$ (2)

where a is a slope, b is an intercept for the linear regression.

The second calibration procedure was based on the relationship between the ratio of the analyte to the Compton peak intensities (I_i/I_{inc}) and the reference concentrations:

$$C_i = a \cdot I_i/I_{inc} + b$$ (3)