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

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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.

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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.

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$_\alpha$-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.
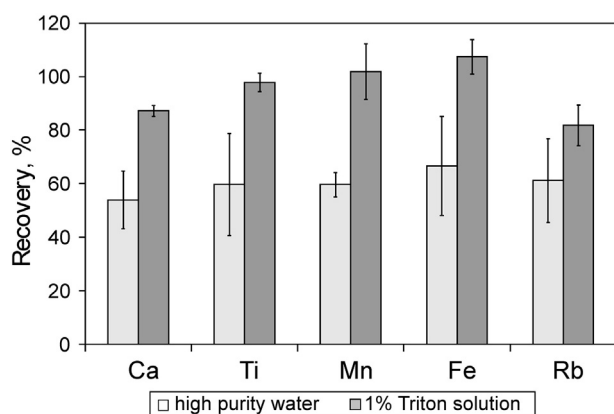
Fig. 1. The recovery data obtained for different conditions of the granite RM G-2 preparation (error bars represent the standard deviation of three replicates measured twice).
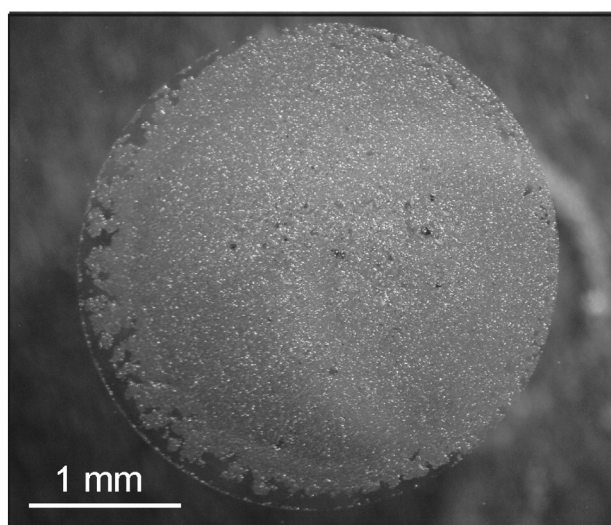

Fig. 2. Image of the RM G-2 pipetted on the sample carrier, which has been obtained using an optical microscope.

The granite RM G-2 was used for the choice of dispersing agents. The sample weight was 50 mg. Two dispersants such as high-purity water and aqueous 1% Triton X-100 solution were tested for the suspension preparation. Fig. 1 demonstrates that the usage of the Triton X-100 solution as the dispersant gives good results for all elements determined, so the recovery data are improved. Furthermore, the Triton X-100 solution provides the homogeneity of the analyzed samples. Fig. 2 demonstrates

an image of the granite RM G-2 suspension obtained by the Triton X-100 solution and pipetted on the sample carrier. The image has been obtained using an optical microscope. The size of the suspension spot on the sample carrier surface is 3 mm. It is seen that the powder particles are uniformly distributed in the volume of the suspension.

The manganese ores have a high bulk density (4.5 g/cm^3) and total content of metals. Preparation of homogeneous and stable suspension of these ore samples is a difficult task due to the fast sample sedimentation on the bottom of the tube. We considered the following approach to the ore sample preparation for TXRF. As an example, the oxydic manganese ore RM 5406-90 was used. Three different dispersants such as high-purity water, the 1% Triton X-100 solution, and mixture of 5% HNO$_3$ acid with 0.1% Triton X-100 solution were tested for the ore suspension preparation. Different sample weights such as 10, 20, 50, and 100 mg were mixed with 10 ml of each dispersant.

Effect of the sample amount and different dispersing agents on the TXRF results was studied. The recovery data obtained for different conditions of the manganese ore RM 5406-90 preparation are presented in Fig. 3. As it can be seen, using high purity water as diluting agent prevents obtaining the stable suspension and all TXRF results were underestimated. The solution of Triton X-100 is a stabilizing reagent, so its addition prevents the sedimentation of particles on the bottom of the tube. Fig. 3 shows that the recovery data are improved when the Triton X-100 solution or the mixing of nitric acid and the Triton X-100 are used. Preparing a suspension with the Triton X-100 solution is a more simple procedure and it gives good results for the most elements determined. Similar results were obtained when 10, 20 or 50 mg of the same sample was suspended in 10 ml of the Triton X-100 solution. When sample weight was 100 mg, the most of the TXRF results were underestimated, probably due to the broken condition of thin layer.

3.1.2. TXRF spectra of solid samples

Fig. 4 demonstrates the X-ray spectrum obtained from the granite RM G-2 suspension in K K$_\alpha$ (3.313 keV) to Y K$_\alpha$ (14.957 keV) energy range. The certified contents of the elements determined in the RM G-2 were taken from [30]. For the estimation of major and trace element concentrations, the spectral line overlaps of the elements determined were taken into account using Spectra software [23]. As can be seen from Fig. 4, the Ti K$_\alpha$ (4.510 keV), Cs L$_\alpha$ (4.286 keV), and La L$_\alpha$ (4.651 keV) lines overlap on the Ba L$_\alpha$ (4.467 keV) line. Also, the As K$_\alpha$ (10.543 keV) line overlaps on the Pb L$_\alpha$ (10.549 keV) line. Furthermore, the Rb K$_\alpha$ (13.394 keV) line overlaps on the U L$_\alpha$ (13.613) line.

Values of Ti, Cs, La, and Ba concentrations in granites and granitoids vary within wide ranges (in mg/kg): 1000–5000, 1–100, 10–200, 10–2000, respectively. The average concentrations of As, Pb, Rb, and U in granites are about 2, 30, 150, 4 mg/kg, respectively.

Fig. 5 displays the X-ray spectrum obtained from the apatite sample CL-1 in K K$_\alpha$ (3.313 keV) to Y K$_\alpha$ (14.957 keV) energy range. As can be seen from the figure, in addition to the aforecited overlaps, the effect
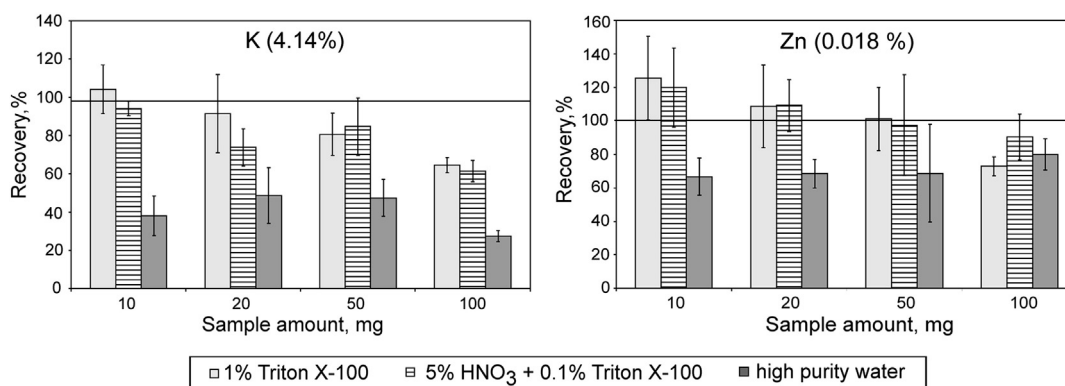

Fig. 3. The recovery data obtained for different conditions of the manganese ore RM 5406-90 preparation (error bars represent the standard deviation of three replicates measured twice).
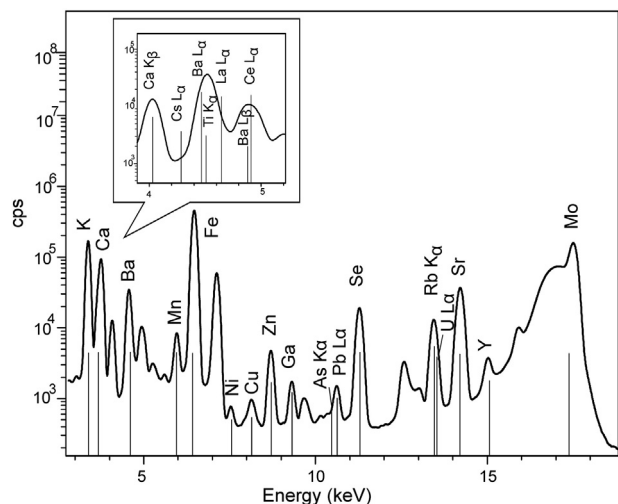
Fig. 4. TXRF spectrum of the granite RM G-2 suspension in K K_α–Y K_α energy ranges from 4 to 18 keV. In this figure the plot of the X-ray spectrum in energy range from 4 to 5 keV is separated (analytical conditions: sample amount − 50 mg, Se concentration − 200 ppm, sample volume − 10 μl, measuring time − 1000 s).

of the Ti K_β (4.933 keV) line on the V K_α (4.945 keV) line should be carefully accounted.

Fig. 6 demonstrates the X-ray spectrum for the oxydic manganese ore RM 5406-90 suspension in K K_α (3.313 keV) to Y K_α (14.957 keV) energy range. This suspension was obtained by mixing 20 mg of the sample amount with 10 ml of the 1% Triton X-100 solution. It is seen that high peaks of Mn, Fe, Ba, and Pb in the spectrum are observed. The certified contents of Mn, Fe, Ba, and Pb are equal to 15.98, 2.43, 2.65, and 0.23%, respectively [29].

3.1.3. Statistical analysis

Analytical figures of merit such as total uncertainty, accuracy of the element determination, and the detection limits (DLs) were carefully studied, as exemplified by the rock and mineral CRMs and RMs. The total uncertainty (the variance V_Σ) was divided into two components [31]:

$$V_\Sigma^2 = V_R^2 + V_P^2, \tag{1}$$

where V_R is the variance, characterizing the reproducibility of the measurement of an analytical signal from one sample; V_P is the variance, characterizing the stability of the sample preparation conditions from the same specimen, including the addition of the internal standard.

The values of the components V_P and V_R were evaluated as well as in [2]. The statistical processing of the analytical results was performed in
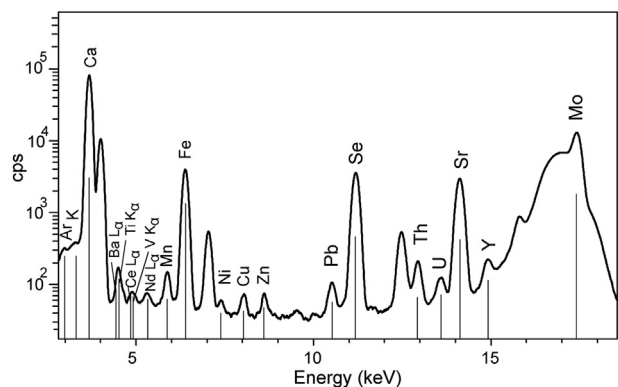

Fig. 5. TXRF spectrum of the apatite sample CL-1 suspension in K K_α–Y K_α energy ranges from 4 to 18 keV (analytical conditions: sample amount − 10 mg, Se concentration − 200 ppm, sample volume 10 μl, measuring time − 1000 s).

Fig. 6. TXRF spectrum of the oxydic manganese ore RM 5406-90 suspension in K K_α–Y K_α energy ranges from 4 to 18 keV (analytical conditions: sample amount − 20 mg, Se concentration − 1000 ppm, sample volume − 10 μl, measuring time − 1000 s).
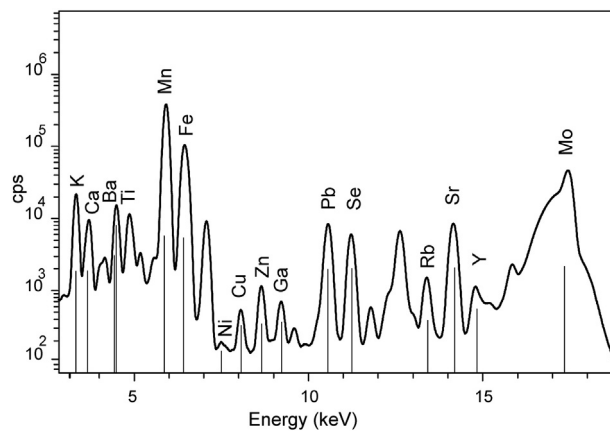
accordance with the recommendations given at the confidence level P = 0.95 [32]. The variances of the total uncertainties for the analyzed samples are within the interval from 6 to 11% for Sr, Rb, Pb, Ba, and Cs in the K-feldspars, and from 3 to 12% for V, Cu, Zn, Rb, Sr, Y, Ba, La, Ce, Pr, Nd, Gd, Pb, and U in the apatites. The values of the total uncertainty V_Σ do not exceed the values of the permissible standard deviation σ_r [33].

3.1.4. Detection limits

The detection limit of the element determined for the suspensions of all geological CRMs and RMs was estimated according to the 3σ approach:

$$DL = 3 \times \sigma_{blank} \times (C/N_{net}), \tag{2}$$

where σ_{blank} is the square root of the background area under the respective peak of the element (count rate), N_{net} is the net intensity (count rate), and C is the certified value of the concentration of the element in the CRM.

The effect of the sample amount on the TXRF results and the DLs was assessed. Generally, increasing the sample amount enables us to enhance the DLs of the elements determined in 3–5 times. In Fig. 7 the effect of different sample amounts (10–100 mg) on the DLs of Ca, Ba, Th, and Pb using the RM JG-2 is displayed. It can be seen that the values of the DLs are significantly decreased for all elements when augmenting the sample weight. It is necessary to note that high mass of the analyzed sample (more than 50 mg) brings about the appearance of the absorption effects in the low-energy range of the spectrum (Z < 20) and the recovery data for K and Ca are getting worse (Fig. 8). As shown in Fig. 8,
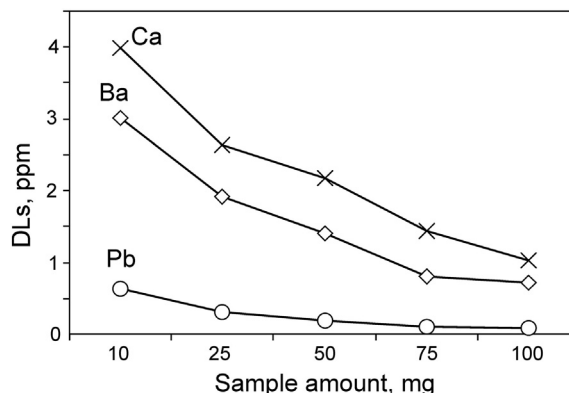

Fig. 7. Effect of sample amounts of RM JG-2 on the detection limits (DLs) for Ca, Ba, and Pb.
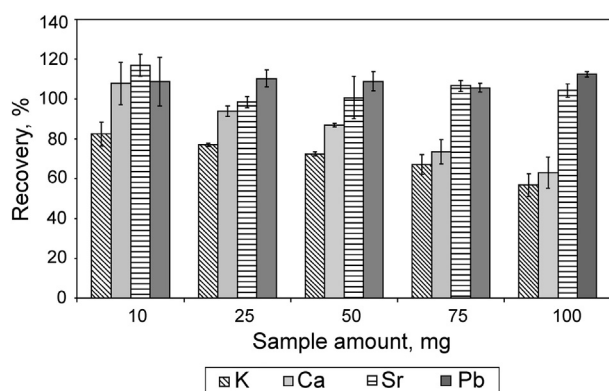
Fig. 8. Effect of sample amounts of RM JG-2 on the TXRF results (error bars represent the standard deviation of three replicates measured twice).

the recovery values for trace elements Sr, Ba, and Pb slightly depend on the sample amount and approximately equal to 100%.

The DLs assessed for some major, trace, and rare earth elements in the rock RMs JG-1, JG-2, and JF-1 are presented in Table 1. As it can be seen, the DLs vary from 0.2 to 11 mg/kg depending on the element and their content in the sample. The DLs estimated for K, Ca, Ti, Mn, Fe, Zn, Ba, and Pb in the ore RM 5406-90 are 13, 18, 7, 7, 5, 1, 18, and 1 mg/kg, respectively.

The values of the DLs, which assessed from the expression 2 and displayed in Table 1, do not account the uncertainties of the measurement and the sample preparation. The DLs for the whole analytical procedure can be calculated using blanks prepared from silicon dioxide powders according to the sample preparation procedure [31]. If the σ_{blank} value is estimated as standard deviation of the results of the background measurements of the blanks, then the calculated values of the DLs are increased in 3–5 times [2].

3.1.5. Accuracy of the element determinations

The accuracy of some major and trace element determinations in the samples studied was checked using the RMs, such as JF-1 and AK 2462-82 [30,34]. The obtained TXRF results are summarized in Table 2. It is necessary to note that the certified values for Pr and U in RM JF-1, and for V, Zn, Ba, Pb, U in RM AK 2462-82 are below the detection limit values for these elements (see Table 1). As it follows from Table 2, the values of the discrepancies between the TXRF results and the certified values are less than 10%.

The comparison between the TXRF and the ICP-MS results obtained for apatite sample CL-1 has been carried out (Fig. 9). This figure shows a

Table 2
The TXRF results of the element determinations in JF-1 and AK 2462-82 RMs.

Element	JF-1		AK 2462-82	
	C ± Δ, mg/kg	Reference value, mg/kg	C ± Δ, mg/kg	Reference value, mg/kg
K	76,840 ± 620	83,596	1720 ± 180	1800
Ca	7886 ± 205	6575	469,900 ± 31,880	506,600
V	2.9 ± 0.2	3	<DL	Not certified
Cu	0.7 ± 0.2	0.2	35 ± 3	Not certified
Zn	2.7 ± 0.18	3.2	<DL	Not certified
Rb	238 ± 23	264	33 ± 2	Not certified
Sr	156 ± 8	163	22,483 ± 562	22,300
Y	3 ± 0.75	2.99	340 ± 23	320
Ba	1645 ± 121	1680	<DL	Not certified
La	2.5 ± 0.16	2.86	2031 ± 136	2040
Ce	4.6 ± 1.2	4.11	3060 ± 280	2930
Pr	<DL	0.5	370 ± 40	340
Nd	2 ± 0.5	1.44	1153 ± 67	1200
Gd	1.4 ± 0.1	1.1	154 ± 15	190
Pb	36 ± 3	33.4	<DL	Not certified
U	<DL	0.33	<DL	Not certified

good agreement for all elements determined. The values of the discrepancies between the TXRF and the ICP-MS results are less than the permissible standard deviation σ_r, yielding the third category of the precision of the mineral raw material analysis [33].

3.2. TXRF analysis of water samples

Mass fraction of TDS, which comprises largely inorganic salts (HCO_3^-, Ca^{2+}, Cl^-, Mg^{2+}, Na^+, SO_4^{2-}), can vary from 0.01 g/l up to 400 g/l and significantly determines the capabilities and limitations of the direct TXRF. The number of the elements determined and the DLs are also dependent on the genesis of the formation of water, e.g. ground, surface or atmospheric waters. For instance, ground waters, whose sample spectrum is shown in Fig. 10, are usually enriched with Fe, Mn, Sr, Ba, etc. in comparison with other waters. In our laboratory the evaluation of different factors affecting the TXRF results of different types of waters have been performed [35].

Using the scheme of single-factor analysis the total uncertainty of the TXRF results (the variance V_Σ) [2] was evaluated for the ground water sample deposited on the hydrophobic and the non-hydrophobic surfaces of the carriers. It was obtained that the value of V_Σ is mainly influenced by the instability of sample preparation conditions. When using the non-hydrophobic carriers the values of V_Σ were 11, 12, 16, 9, 10, 28, 36, 16, 13, 11, and 55% for S, Cl, K, Ca, Mn, Ni, Cu, Zn, Br, Sr, and Ba, respectively. This is due to the spreading of droplet, its non-uniform

Table 1
Detection limits assessed for some trace and RE elements in the rock RMs.

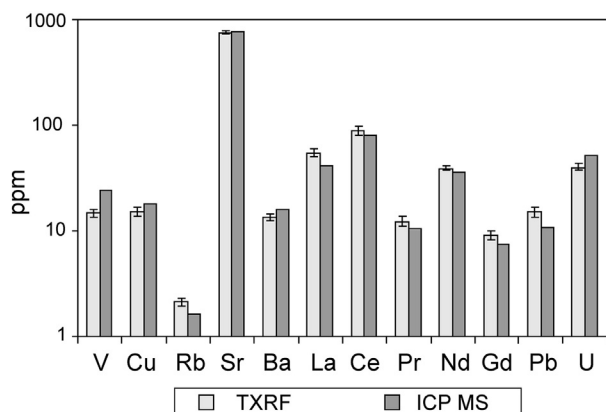| Element	Range, mg/kg	Apatite RMs, mg/kg (10 mg in 2.5 ml of Triton X-100 solution)	K-feldspar RMs, mg/kg (50 mg in 2.5 ml of Triton X-100 solution)
K	1600–131,100	9.2	10.8
Ca	900–506,600	1.2	8.0
V	3–500	2.0	0.2
Cu	2–100	0.8	0.3
Zn	1–100	0.4	0.6
Rb	2–200	0.4	0.2
Sr	10–22,000	0.8	0.2
Y	10–320	0.7	0.3
Cs	20–3000	7.2	11
Ba	10–1000	5.0	1.6
La	20–2000	4.0	1.8
Ce	40–3000	4.0	1.1
Pr	6–340	3.0	2.5
Nd	30–1200	3.0	0.8
Gd	7–200	0.2	0.6
Pb	6–50	0.7	0.2
U	2–40	1.0	0.7

Fig. 9. Comparison between the TXRF and the ICP-MS results obtained for apatite sample CL-1 (error bars represent the standard deviation of three replicates measured twice).

Fig. 11. Effect of the brine dilution on the results of Cl, K, Ca, Br, and Sr determinations (error bars represent the standard deviation of three replicates measured twice).

drying on the non-hydrophobic carrier, and a large area of the spot of dried residue. The hydrophobization of the carrier surface reduces the error of the analysis 2–3 times (S − 6%, Cl − 3%, K − 6%, Ca − 4%, Mn − 9%, Ni − 14%, Cu − 11%, Zn − 9%, Br − 4%, Sr − 4%, Ba − 25%).

If 10 μl of a water sample is pipetted on the siliconized carrier, the dried residue of 2–3 mm in diameter is formed. The theoretical estimates of the critical thickness were performed taking into account the internal standard of Ga [8]. It was demonstrated that in the determining elements in the low-energy X-ray range of the spectrum (e.g. S, Cl, K, Ca) the significant matrix effects are observed for waters of the TDS more than 2–5 g/l [35]. In the high-energy X-ray range of the spectrum (Z > 20) the effect of the TDS is less significant, provided that the analyte and the internal standard are homogeneously distributed in the sample.

It was shown on the example of sodium-chloride brines that to achieve the formation of homogeneous and suitable thickness of the sample onto the carrier it is necessary to dilute the high-mineralized water with the 1% solution of Triton X-100 to eliminate the self-absorption effects in determining the major elements. The addition of the Triton X-100 allows one to reduce the viscosity of the solution and makes the emitting layer thinner due to stopping the crystallization process and a more uniform distribution of particles on the carrier surface [35]. The effect of the dilution ratio on the TXRF results of Cl, K, Ca, Br and Sr determination is demonstrated in Fig. 11. As it can be seen, when analyzing slightly diluted sample the recoveries of the TXRF results were very low because of the saturation effects. A good agreement (the discrepancies were less than 10%) between the results of TXRF and chemical analysis was obtained for Cl, K, Ca, Br, and Sr at
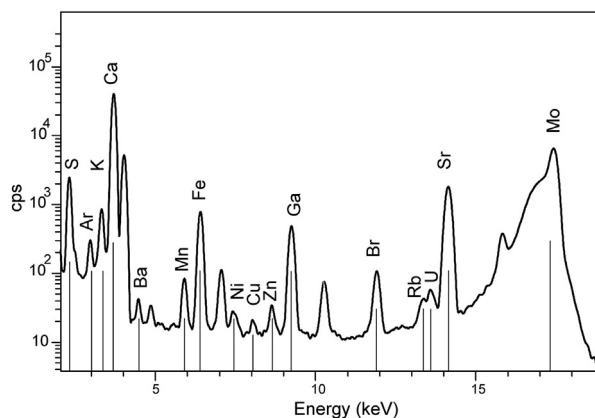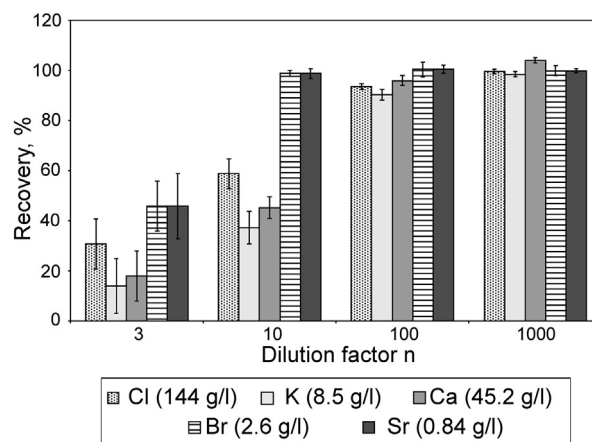
the dilution 100–1000 times. The Rb contents, varying from 13 to 22 mg/l, according to chemical analysis, were not determined in the brines because of the high Br content (2400–3500 mg/l) and the overlapping Br K_β (13.29 keV) and Rb K_α (13.39 keV) lines.

To estimate the effect of the TDS contents on the DLs of trace elements, the model solutions with different mineral contents (32,000, 3200, 320, and 32 mg/l) were used. Fig. 12 presents the dependences of the detection limits on the atomic number Z for different salt solutions. One can see that at TDS ≤ 3200 mg/l the detection limits depend little on the matrix concentrations and vary from 6 to 0.6 μg/l depending on Z. It should be taken into account that the DLs are calculated for the model solutions with equal concentrations of Ti, V, Cr, Mn, Fe, Co, Ni, Cu, As, Se, Tl, and Pb. The spectral interferences of the neighboring elements, whose amounts are significantly different, make the detection and the fitting of low peak to be difficult in the presence of high peak. At high salt contents (TDS = 32 000 mg/l) the DLs increase by a factor of 10–11 for all analytes. Normally, such minimal treatment of high-mineralized samples as the dilution allows one to quantify only major and minor elements. However, the dilution reduces the sensitivity of the detection of small amounts of elements, so for trace and ultra trace determinations in salt waters prior removal of the matrix elements is needed.

Typically, all water samples are acidified (pH < 2) before the analysis to ensure stability. The effect of the acidification was evaluated using the bicarbonate mineral water sample (Fig. 13). It was found that without the acidification the concentrations of Ca (69 mg/l) and Sr (0.67 mg/l) were underestimated by 4–5 times compared with the results obtained by "wet" chemistry for Ca (320 mg/l) and Sr (3 mg/l). But after the acidification the discrepancies between the results obtained by TXRF and
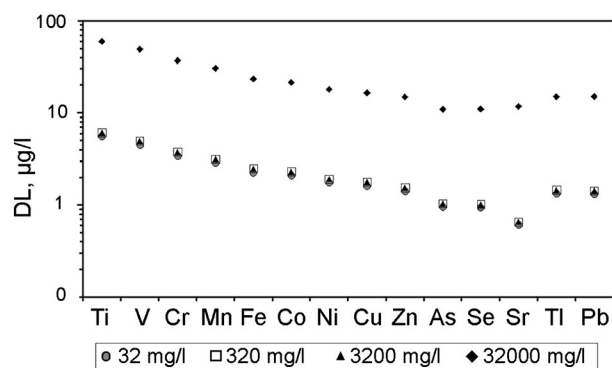

Fig. 10. TXRF spectrum of the ground water sample (analytical conditions: Ga concentration − 200 μg/l, sample volume − 10 μl, measuring time − 1000 s).

Fig. 12. Effect of the salt matrix concentration on the detection limits (DLs) of the trace elements (analytical conditions: sample volume − 10 μl, measuring time − 1000 s).
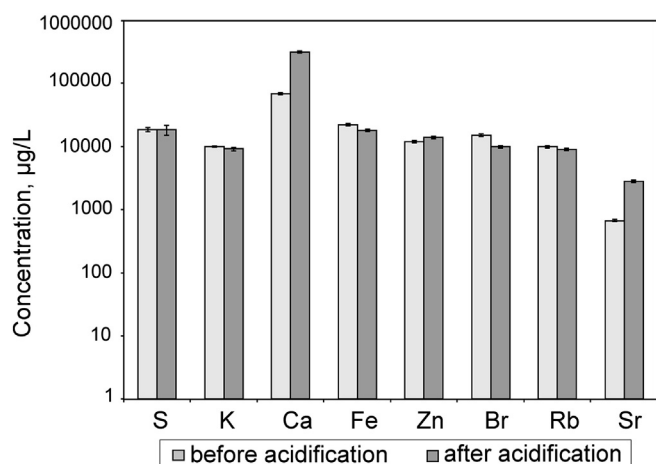
Fig. 13. Effect of the acidification of the bicarbonate mineral water sample on the TXRF results.

chemical analysis were less than 10%. For other elements this effect was less significant. This is probably due to the fact that the non-acidified sample drying results in calcium and strontium bicarbonates crystallization in the form insoluble carbonates, so the internal standard and the sample can be spatially separated. The acidification of the water sample prevents the precipitation of carbonates.

Normally, fresh water samples can be analyzed by TXRF without any treatment. However, analysis of waters with low element contents requires the special cleanliness of analytical work place. The contaminations with traces of Fe, Cu, and Zn in the process of the sample preparation and the measurement could become significant. Comparing the analytical results obtained by TXRF and ICP-MS in some samples showed that the concentrations of Fe, Cu, and Zn were too high. In this case, we recommend preparing and measuring the blanks (quartz carrier and ultrapure water) according to the sample preparation conditions. The spectra of the blanks should be subtracted from the sample spectra using the software SPECTRA 5.3 [23]. Such manipulations allow us to obtain an agreement between the TXRF and the ICP-MS results.

Table 3 gives the examples of the comparison of the element contents in fresh waters determined by ICP-MS and TXRF. The concentrations of the TXRF results were calculated on the basis of triplicate determinations. The variation coefficients that characterize the discrepancy between the results obtained by these methods are less than 15% for most elements, but in case of the low concentrations it can reach 20–30% and more.

4. Conclusion

In this work various types of geological and environmental samples such as rock, mineral, ore and natural water samples were thoroughly

studied. The effect of different factors on the TXRF results obtained using minimal sample pretreatment was evaluated. It was shown that the preparation of the suspensions from the rock, mineral and ore powders with the Triton X-100 solution is a simple fast procedure, which can be successfully used in geological studies, especially in cases when it is necessary to analyze samples of limited mass. For obtaining reliable TXRF results a mass of powder must be controlled. For the K-feldspars and apatites the powder weighing 10–50 mg should be suspended in 2.5 ml of the 1% Triton X-100 solution. For the ore samples having high bulk density and metal amounts the volume of the 1% Triton X-100 solution should be increased to 10 ml for the weighing 10–50 mg. For all samples, mass more than 50 mg leads to the absorption effects in the low-energy range of the spectrum. The total uncertainty V_Σ has been evaluated for the rocks and minerals. The values of V_Σ do not exceed the values of the permissible standard deviation σ_r when determining the element contents in the range of 0.0001–0.2%.

In case of natural water samples it is necessary to take into account TDS content. Water of low salinity can be measured directly. However, there is a need to siliconize a quartz carrier and have clean laboratory conditions. As exemplified by the bicarbonate mineral water sample it was demonstrated that acidification of the water sample prevents the precipitation of carbonates. Water of high TDS (>2–5 g/l) should be diluted with the 1% solution of Triton X-100. It is imported to remark that such sample preparation procedure allows one to quantify only major and minor elements.

Although direct TXRF has limited sensitivity for some elements, it can be applied in geological and environmental studies. It should be taken into account that analytical possibilities of TXRF and figures of merit, presented in the work, strictly depend on physical–chemical features of analyzed objects and sample preparation conditions. Producing a sample homogeneous layer and avoiding contamination during the sample preparation and the measurement allow one to obtain the TXRF results comparable with those of other commonly used methods.

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Table 3
Comparison of the results (μg/l) obtained by TXRF and ICP-MS techniques.

Element	Sample 1		Sample 2		Sample 3	
	TXRF	ICP-MS	TXRF	ICP-MS	TXRF	ICP-MS
S	1866 ± 126	1814 ± 100	1970 ± 50	1711 ± 80	25,755 ± 1030	33,261 ± 1600
K	1188 ± 40	1021 ± 20	1055 ± 20	889 ± 17	3555 ± 130	3841 ± 70
Ca	14,600 ± 470	14,235 ± 280	16,100 ± 150	15,702 ± 310	55,850 ± 1460	68,155 ± 300
Mn	45 ± 2	42 ± 1	6.0 ± 0.7	4.5 ± 0.2	175 ± 10	182 ± 5
Fe	7.0 ± 3.0	4.2 ± 0.5	<DL	2.8 ± 0.3	35 ± 11	52 ± 6
Ni	0.70 ± 0.20	0.58 ± 0.06	<DL	0.16 ± 0.02	7.7 ± 0.8	7.6 ± 0.8
Zn	8.1 ± 0.5	7.2 ± 0.5	2.0 ± 0.5	1.6 ± 0.1	79 ± 5	91 ± 6
Br	6.0 ± 0.4	5.8 ± 0.3	6.0 ± 0.3	6.0 ± 0.3	30 ± 1.0	29 ± 1.5
Rb	0.70 ± 0.10	0.66 ± 0.02	0.70 ± 0.10	0.53 ± 0.02	2.0 ± 0.5	1.53 ± 0.04
Sr	107 ± 2	93 ± 5	106 ± 2	95 ± 5	298 ± 9	306 ± 17
Ba	10 ± 2	8.8 ± 0.5	8.2 ± 2	9.6 ± 0.5	58 ± 12	75 ± 5

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