



APPLICATION OF TOTAL-REFLECTION X-RAY FLUORESCENCE SPECTROMETRY (TXRF) TO GEOLOGICAL OBJECTS: EXPERIENCE OF THE TXRF LABORATORY, CENTRE FOR GEODYNAMICS AND GEOCHRONOLOGY

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ABSTRACT. Unlike conventional X-ray fluorescence spectrometry, the total-reflection X-ray fluorescence spectrometry is not a widespread and routine method for analyzing solid samples with mineral matrix, but it has a great potential for geochemical, geological, and archaeological studies. Rapid multi-elemental analysis of very small sample amounts can be performed by the internal standard method which does not require the-matrix-matched reference materials. This is an undoubted advantage of the TXRF method over the conventional X-ray fluorescence method, especially if there is a limited available sample amount and a lack of well-characterized reference materials. This paper presents our experience with the application of TXRF spectrometry in the elemental analysis of apatite, ceramics, sediments, ores, and nodules. Special attention has been paid to the sample preparation procedure because it is one of the main sources of errors in the analysis. Preparing thin homogeneous specimen from the solid sample with a complex mineral matrix is not easy. Sample preparation strategy should be chosen considering the features of an analytical object, the content of the elements to be determined, and the accuracy required for a reliable interpretation. Consideration is being given to the examples of the preparation of a suspension for rapid analysis of ores and sediments, and to the original techniques of chemical decomposition for apatite and ceramics.

KEYWORDS: total-reflection X-ray fluorescence; multi-elemental analysis; sample preparation; accuracy assessment; apatite; ores; nodules; ceramics; sediments

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ПРИМЕНЕНИЕ МЕТОДА РЕНТГЕНОФЛУОРЕСЦЕНТНОЙ СПЕКТРОМЕТРИИ С ПОЛНЫМ ВНЕШНИМ ОТРАЖЕНИЕМ (TXRF) К ГЕОЛОГИЧЕСКИМ ОБЪЕКТАМ: ОПЫТ ЛАБОРАТОРИИ TXRF (ЦКП «ГЕОДИНАМИКА И ГЕОХРОНОЛОГИЯ»)

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АННОТАЦИЯ. В отличие от традиционной рентгенофлуоресцентной спектрометрии, рентгенофлуоресцентная спектрометрия с полным внешним отражением не является распространенным и рутинным методом анализа твердых образцов с минеральной матрицей, но имеет большой потенциал для геохимических, геологических и археологических исследований. Быстрый многоэлементный анализ очень малого количества образца может быть выполнен с помощью способа внутреннего стандарта, который не требует стандартных образцов для калибровки. Это несомненное преимущество метода TXRF по сравнению с традиционным рентгенофлуоресцентным методом, особенно при ограниченном количестве доступного материала объекта и отсутствии подходящих эталонных образцов. В этой статье представлен наш опыт применения TXRF-спектрометрии для элементного анализа апатита, керамики, осадков, руд и конкреций. Особое внимание уделено процедуре пробоподготовки, поскольку она является одним из основных источников ошибок при анализе. Приготовить тонкий однородный образец из твердого образца со сложной минеральной матрицей непросто. Стратегию пробоподготовки следует выбирать с учетом особенностей аналитического объекта, содержания определяемых элементов и точности, необходимой для надежной интерпретации. Рассмотрены примеры приготовления суспензии для экспресс-анализа руд и осадков, оригинальные процедуры химического разложения апатита и керамики.

КЛЮЧЕВЫЕ СЛОВА: рентгенофлуоресцентный анализ с полным внешним отражением; многоэлементный анализ; пробоподготовка; оценка точности; апатит; руды; конкреции; керамика; осадки

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1. INTRODUCTION

Total-reflection X-ray spectrometry (TXRF) is currently one of the few analytical methods providing a rapid and cost-efficient multi-elemental analysis of various liquid and solid samples. TXRF is a variation of the energy dispersive X-ray fluorescence (XRF). It was first described in 1971 by Yoneda and Horiuchi [Yoneda, Horiuchi, 1971], who used the total reflection of X-rays discovered by Compton in 1923 [Compton, 1923] to analyze small amounts of sample on optically flat surfaces. The main parts of an energy dispersive spectrometer are an X-ray tube, a monochromator, and a detector. Fig. 1 presents the principle scheme of TXRF. The essential difference between TXRF and conventional XRF is in the special geometry of the X-ray tube and detector. Unlike XRF, where the primary X-ray beam is directed at 45°, the X-ray beam in the TXRF spectrometer hits the sample on the carrier at a very small angle and is almost totally reflected therefrom. X-ray fluorescence radiation is detected by a silicon-lithium or silicon drift detector. The detector is placed at a very small distance directly above the sample to record the characteristic radiation. Only a small amount of sample is allowed to avoid limiting the total reflection and blocking the detector [Klockenkämper, von Bohlen, 2015].

The main advantages of TXRF as compared to other spectral methods are as follows:

- A small volume of the sample required (μL - mL or μg - mg range);

- A variety of sample preparation procedures (minimal sample pretreatment by direct analysis, decomposition of matrix, preconcentration or extraction);

- Quantification by the internal standard method (no external calibration is required);

- Fast screening (semi-quantitative and quantitative multi-elemental analysis within 200–1000 s);

- Low operational cost (no cooling media and gas consumption).

Currently, different commercial TXRF spectrometers are available on the market and there are many examples of

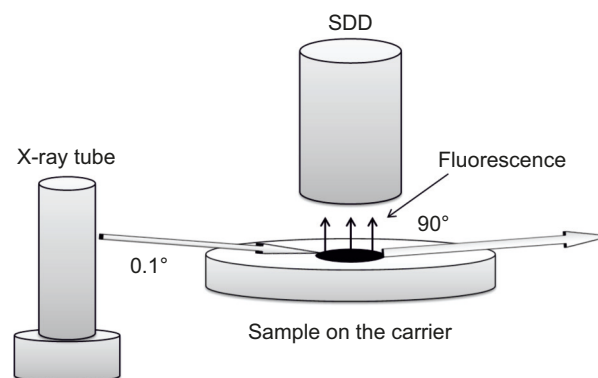


Fig. 1. Principle scheme of TXRF (SDD is silicon drift detector).

Рис. 1. Принципиальная схема TXRF (SDD – кремниевый дрейфовый детектор).

applying this method to different objects, especially liquids and biological materials. However, unlike conventional XRF or atomic absorption or emission spectral methods, TXRF is not a popular method for the analysis of geological materials, especially in Russia. Due to the above-mentioned advantages, TXRF has a great potential in geochemical, geological, and archaeological studies but special sample preparation procedures should be performed.

The S2 PICOFOX (Bruker Nano GmbH, Germany), a benchtop spectrometer, has been used in the TXRF laboratory of the Centre for Geodynamics and Geochronology since 2009. Initially, the TXRF laboratory was specialized in the analysis of liquid samples as water [Pashkova, Revenko, 2013a, 2013b, 2015; Pashkova et al., 2013], brines [Pashkova, Revenko, 2015; Pashkova et al., 2013], milk [Smagunova, Pashkova, 2013; Pashkova et al., 2018b], tea [Maltsev et al., 2019a, 2021a], and beverages [Maltsev et al., 2019b, 2022]. Nowadays we also use TXRF for different solid samples with a complex mineral matrix. This paper aims to present our experience with the application of TXRF spectrometry in the elemental analysis of apatite, ceramics, sediments, ores, and nodules.

2. APPLICATION OF TXRF TO GEOLOGICAL OBJECTS

General procedures for preparing solid samples are presented in Fig. 2. Fast sample preparation techniques are called "direct" analysis including the semi-quantitative technique of "deposition of particles" and suspension preparation: the latter is the most popular among TXRF users. Mineralization techniques are more time- and reagent-consuming but remain more reliable in terms of the accuracy of measurement. The disadvantage of the mineralization technique is the probability of inaccurate determination of the volatile elements S, Cl, Br, As, due to full or partial evaporation losses that's why in this case the direct analysis is preferable. Extraction procedures are used when the sensitivity of TXRF is restricted for some of the elements (rare-earth elements REE, for example) or there are spectral interference issues caused by a high intensity of matrix elements. The TXRF methods developed by the researchers of the TXRF laboratory (Centre for Geodynamics

and Geochronology) for different geological samples are presented in Table 1.

Two TXRF methods for the multi-element analysis of apatite were developed and validated, one is for large crystals (size of 1–2 mm) and another for microcrystals (size of 50–100 μm) [Maltsev et al., 2020, 2021b]. The acid digestion strategy was preferable for both of methods with lower detection limits and better precision values as compared to suspension preparation. **Apatite** elemental content was determined by TXRF in the provenance study of Slyudyanka apatite and for a fission-track study. As is known, some apatite samples are rich in REE and As, Sr, Th, U, etc., and it was shown that TXRF is a well-suitable method for the determination of these elements. Moreover, the advantage of TXRF compared to the routine laser ablation inductively coupled plasma mass spectrometry (LA-ICP-MS) is a reliable quantitative analysis. The methods were validated through combined procedures: analysis of Durango and Otter Lake well-known apatite samples; using inductively coupled plasma mass spectrometry (ICP-MS) and wavelength-dispersive X-ray fluorescence spectrometry (WDXRF) as reference analytical methods; assessment of the measurement uncertainty.

TXRF can be applied for direct analysis of iron, manganese, ferromanganese, nickel-copper sulfide **ores**, oceanic and lacustrine **nodules** [Pashkova et al., 2020; Akhmetzhanov et al., 2021; Chubarov et al., 2021]. The suspension preparation (5 mL of 1 % Triton X-100 solution and 20 mg of fine powder with a size $<10 \mu\text{m}$ and internal standard of Ga) gives a possibility for fast reliable determination of major and minor elements by the internal standard method with the recovery values 75–125 %. The determination of trace elements in an ore matrix without preconcentration procedures can only be considered as semi-quantitative. It was shown that the reproducibility of direct TXRF analysis strongly depends on the particle size in the analyzed powder. The poor reproducibility values ($>15 \%$) were observed for samples with an average particle size of more than $10 \mu\text{m}$, so that a thorough additional grinding of powder before the suspension preparation is required. Dry mechanical grinding allows obtaining the powder with

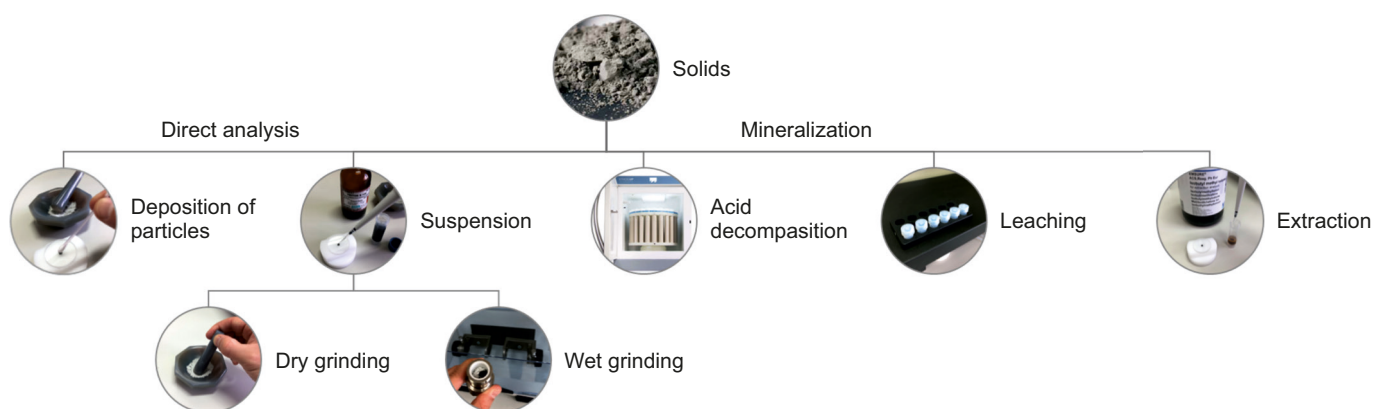


Fig. 2. Sample preparation scheme for TXRF analysis of solid materials.

Рис. 2. Схема пробоподготовки для TXRF-анализа твердых материалов

Table 1. Description of TXRF methods developed by researchers of TXRF laboratory (Centre for Geodynamics and Geochronology)
Таблица 1. Описание методик TXRF, разработанных сотрудниками лаборатории TXRF (ЦКП «Геодинамика и геохронология»)

Sample type	Sample preparation	Elements	Calibration	Concentration range	Validation	LOD, mg/kg	Reference
Apatite	Digestion: 10 mg of sample + 0.1 mL HNO ₃ , heating and dissolution. 10 µL deposition on a quartz carrier, drying on a hotplate	K, Mn, Fe, Ni, As, Br, Y, Sr, La, Ce, Pr, Nd, Pb, Th, U	Internal standard (Ga)	5–6000 mg/kg	Durango and Otter Lake reference materials, WDXRF and ICP-MS	0.5–3.0	[Maltsev et al., 2020]
	Digestion: few µg of sample + 0.5 µL HNO ₃ , directly on a quartz carrier, heating, dissolution, and drying on a hotplate		Internal standard (P)			1.0–20	[Maltsev et al., 2021b]
Ores and nodules	Suspension: 20 mg of sample + 5 mL 1 % Triton X-100. 10 µL deposition on a quartz carrier, drying on a hotplate	S, K, Ca, Ti, V, Mn, Fe, Co, Ni, Cu, Zn, As, Sr, Y, Pb	Internal standard (Ga)	mg/kg – %	19 CRMs of ores and nodules	nd	[Pashkova et al., 2020; Chubarov et al., 2021]
Ceramics	Suspension (wet grinding): 20 mg of sample + ultrapure water, mixing in a grinding system. 5 µL deposition on a quartz carrier, drying on a hotplate	Al, K, Ca, Ti, V, Cr, Mn, Fe, Ni, Cu, Zn, Ga, Rb, Sr, Y, Ba, Pb	Internal standard (Ga)	0.1–8.8 % for Z<20 7–1000 mg/kg for trace elements	CRM GeoPT33 (Ball Clay) ICP-MS, WDXRF Interlaboratory study	nd	[Maltsev et al., 2021c; Pashkova et al., 2021]
	Acid leaching: 20 mg of sample + 1.0 mL aqua regia, heating and dissolution. 10 µL deposition on a quartz carrier, drying on a hotplate		Internal standard (Se)				
Sediments	Suspension: 20 mg of sample + 5 mL 1 % Triton X-100. 10 µL deposition on a quartz carrier, air-drying	Br	Internal standard (Ge)	3–20 mg/kg	CRMs of silts and sediments	0.4	[Pashkova et al., 2016]
			Al, K, Ca, Ti, V, Cr, Mn, Fe, Ni, Cu, Zn, Rb, Sr, Ba	Internal standard (Ga); external calibration		0.2–13 % for major elements 12–860 mg/kg for trace elements	nd

Note. CRM – certified reference material, LOD – limit of detection, ICP-MS – inductively coupled plasma mass spectrometry, WDXRF – wavelength-dispersive X-ray fluorescence spectrometry, nd – not determined (the concentrations of the analytes considered were significantly higher than LOD).

Примечание. CRM – аттестованный эталонный материал, LOD – предел обнаружения, ICP-MS – масс-спектрометрия с индуктивно-связанной плазмой, WDXRF – рентгенофлуоресцентная спектрометрия с дисперсией по длине волны, nd – не определено (концентрации рассматриваемых аналитов были значительно выше LOD).

an average particle size of less than 10 μm , but the distribution of particles is not unimodal, with outliers observed among the measurement results. We have recently applied wet grinding to prepare suspension from sulfide nickel-copper ores. With ZrO_2 grinding balls of a minimum diameter of 1 mm, adding water and the internal standard to the grinding jar of the mixer mill is a good way to achieve a homogeneous suspension with minimal particle size and good distribution of the internal standard. In this case, the reproducibility of the suspension preparation is 3–5 % for major elements in ores and nodules. One of the problems of TXRF analysis is strong peaks overlapping due to poor spectral resolution of the energy-dispersive spectrum. For instance, the differences between the TXRF results and the certified values in CRMs may be more than 30 % for As, Pb, V, Cr, Ba in the nodules due to $\text{PbL}\alpha/\text{AsK}\alpha$, $\text{BaL}\alpha/\text{TiK}\alpha$, $\text{CrK}\alpha/\text{VK}\beta$, $\text{VK}\alpha/\text{TiK}\beta$ lines overlapping [Pashkova et al., 2020; Chubarov et al., 2021]. Chemometric approaches may be used to solve this problem [Akhmetzhanov et al., 2021]. It was shown that the calibration models based on partial least squares and principal component regressions provide a quantitative determination of Ce, La, and Nd content in ores and nodules using the TXRF method.

TXRF was also applied to study the composition of **archaeological ceramics** for the characterization of raw materials and manufacturing processes [Maltsev et al., 2021c; Pashkova et al., 2021]. TXRF may be considered a promising method in archaeology due to its capability to analyze a very small amount of a sample (<20 mg), which is very important for the preservation of archaeological material. Two sample preparation techniques for the TXRF analysis of ceramics were offered: suspensions for a bulk composition of ceramics and acid leaching for the elemental determination of the ceramics' clay component. The method was validated by the analysis of certified reference materials (CRM), comparison of results of TXRF with ICP-MS and WDXRF results, and interlaboratory studies. Application of TXRF method to the archaeological ceramics from Popovsky Lug, Eastern Siberia (Russia) allowed collecting the first data on the elemental composition of these samples. Additionally, the elemental composition of ceramics may be used for the next chemometric processing, which helps to identify the groups of different origins.

TXRF method was developed to analyze **the sediments** from Lake Baikal and Lake Khara-Nur (Russia) for environmental and paleoclimate studies [Pashkova et al., 2016, 2018a]. Samples for multielement analysis were obtained by cutting a sediment core with a certain step. Since the samples are quite limited in volume, the TXRF method is well-suitable for this task. The simple sample preparation based on mixing of 20 mg of milled sediment sample and 2 mL of an aqueous 1 % Triton X-100 solution and consequent quantification by the internal standard of Ga provides fast determination of Ca, Ti, Mn, Fe, Ni, Cu, and Sr. The external calibrations and correction to the Compton peak signal make it possible to compensate some systematic errors and expand the elements set with Al, K, V, Cr, Zn, Rb, and Ba. TXRF method was also applied to the Br determination

in lake sediments with only one difference in quantification procedure: using internal standard of Ge instead of Ga [Pashkova et al., 2016]. The detection limit of Br was 0.4 mg/kg, which is almost two times better than that for the WDXRF method. The TXRF results were validated by the analysis of CRMs of sediments, and the comparison of results to the certified concentrations showed good recovery values. Interpretation of the measured concentration values is possible when the random error of analysis is 2–3 times less than the variations in the contents of the elements throughout the core depth. For most of the elements, the measurement and sample-preparation errors were less than 10–15 %, so the direct TXRF analysis can give information about changes in the element concentration with the core depth.

3. CONCLUSIONS

The brief examples of the application of TXRF demonstrate the potential of this method for geological, geochemical, and archaeological research. Careful preparation of a small volume of solid samples is the main condition for successful analytical measurements using TXRF spectrometry. We believe some new possibilities of TXRF will be found based on our experience.

4. CONTRIBUTION OF THE AUTHORS / ЗАЯВЛЕННЫЙ ВКЛАД АВТОРОВ

The authors contributed equally to this article.

Авторы внесли эквивалентный вклад в подготовку публикации.

5. CONFLICT OF INTERESTS / КОНФЛИКТ ИНТЕРЕСОВ

The authors have no conflicts of interest to declare. The authors have read and agreed to the published version of the manuscript.

Авторы заявляют об отсутствии у них конфликта интересов. Авторы прочитали рукопись и согласны с опубликованной версией.

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