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## Elemental Analysis of Copper-Zinc Ores by Total Reflection X-Ray Fluorescence using Nonaqueous Suspensions

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### ABSTRACT

Novel rapid determination of copper-zinc ore elemental composition by total reflection X-ray fluorescence (TXRF) is proposed. Approaches for solid state sample analysis by TXRF are provided. The sample preparation is chosen to obtain the suspensions in ethylene glycol. The optimum suspension preparation conditions (sample mass, volume of dispersion medium) and the measurement conditions (internal standard element, spectra acquisition time) were determined. The sedimentation stability of suspensions was studied. It was found that the suspensions remain stable for approximately 2 min, which is sufficiently long for the sampling the suspension. The proposed technique allows determining the elemental composition of solid ore samples without sample digestion. The sample preparation time takes approximately 20 min. The relative standard deviation of the analytical results did not exceed 10%.

### ARTICLE HISTORY

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sample preparation; total  
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analysis

## Introduction

Determination of the elemental composition of copper-zinc ores is an important task. Obtaining the operative information on the elemental composition during the process of ore extraction and enrichment allows optimizing technological processes and increasing the efficiency of production (Schlesinger et al. 2011). Receiving the information on the toxic elements is also important for the environment protection. Several authors (Giri, Singh, and Mahato 2017; Liu et al. 2017; Yu et al. 2017) show that tails of copper enrichment processes may become a source of such heavy elements as Pb, As, Ni, Co, Cr, Mn, and leaching of these elements leads to contamination of groundwater and soils.

Modern methods such as inductively coupled plasma atomic emission spectrometry (ICP AES) and atomic absorption spectrometry (AAS) (Lachowicz and Kauszuk 1986; Singh, Jain, and Sindhu 1994; ISO 13547 2014) allow reducing the analysis time significantly. However, a considerable part of time is still spent on preparation of the sample for the analysis; in particular for its dissolution. In this paper, we propose to use the method of total reflection x-ray fluorescence analysis (TXRF) for the determination of elemental composition which has practically the same fast sample preparation procedure as the classic XRF but it is characterized by higher sensitivity

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and no need for standard samples (Klockenkamper and von Bohlen 1996; Wobrauschek 2007; Alov 2011).

TXRF is a modern method for the determination of elemental composition of different kinds of samples. It provides high sensitivity, wide dynamic ranges, simultaneous determination of several elements, and high reproducibility. TXRF is able to analyze solid and liquid (after drying) samples, and due to relatively low influence of matrix effects, it significantly reduces sample preparation time by removing the sample digestion stage (Klockenkamper and von Bohlen 1996; Wobrauschek 2007; Alov 2011).

There are several approaches to the analysis of solid samples by TXRF that include direct sample placement on the reflector (standardless, quantification by internal normalization), sample digestion and drying of solution with internal standard added and preparation of suspensions. Standardless quantification assumes that all elements of the sample were measured or that the concentration of non-detectable (blank matrix) part of the sample is known. The internal standard technique is the most convenient because it does not require sample digestion (Klockenkamper and von Bohlen 1999; Filatova et al. 2016). A suspension of a finely ground sample (10–20  $\mu\text{m}$ ) is prepared, a known amount of an element acting as an internal standard is introduced, a droplet of the resulting suspension is applied to the reflector substrate and dried, and the elemental composition is determined using the internal standard quantification (Cherkashina, Panteeva, and Pashkova 2014; Pashkova et al. 2016).

An important factor responsible for the correctness of the results of analysis is suspension stability. The aggregation stability of suspensions can be enhanced by adding surfactants; non-ionic surfactants such as Triton X-100 and Triton X-114 are often used. Minimal particle sizes achieved in reasonable time are tens of micrometers. So it is hard to prepare the aqueous suspensions with the necessary sedimentation stability. The negative effect of sedimentation seems to be the most significant in case of samples with high density particles and with ununiform composition where different components sediment with different rates.

We have proposed to use the high viscosity liquids (ethylene glycol, glycerol) to obtain stable suspensions of inhomogeneous samples such as coal and coke. In our previous work (Sharanov, Alov, and Zolotov 2016), significant enhancement of suspension stability was shown. So, we have applied the same approach to obtain stable suspensions of copper-zinc ores whose density is 2–3 times higher than for coal and coke.

## Experimental

### *Materials and reagents*

Standard solution of Ni 1 mg/ml (D.I. Mendeleyev Institute for Metrology) and analytical grade ethylene glycol were used in this work.

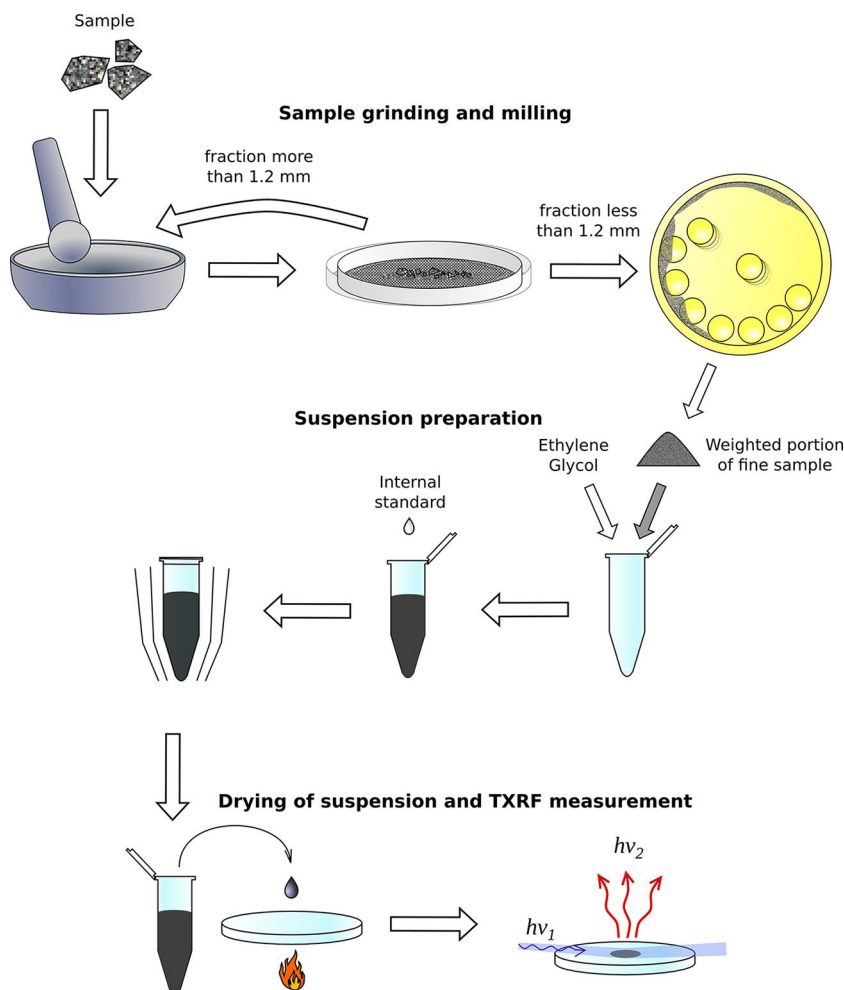
### *Samples*

The samples were obtained from Uchaly copper-zinc ore deposit located in South Ural Mountains, Bashkortostan, Russia. Samples U-1 through U-7 were extracted from working mine at different levels. Samples were acquired from stopped conveyor belt. One meter strip of material across all conveyor belt picked by a shovel to pick up all fractions of ore material. The mass of general samples were 50–70 kg. Samples were successively ground with the mass decreasing using jaw crusher and rod mill until smaller than

10 mm fragments were obtained. This part of primary sample pretreatment was performed on the ore-dressing plant by local personnel.

### **Sample pretreatment**

Sample pretreatment and TXRF measurement procedure are presented in [Figure 1](#). The ore samples (200–300 g, fragments is 10 mm and less) were manually ground in an iron mortar until passing through the 1.2 mm sieves. The sieved fraction was treated with a Pulverisette 7 (Fritsch, Germany) planetary mill using 10 mm zirconium oxide balls in zirconium oxide bowl at 650 rpm for 10 min. A weighed portion of finely milled ore was placed into a polyethylene vial and filled with ethylene glycol. A nickel internal standard was added and the suspension was treated with ultrasonic radiation to destroy ore agglomerates and mixed on a laboratory shaker to obtain a homogeneous mixture. The droplets were sampled by a micropipette and placed on the quartz reflector. The droplet was dried on a hot plate at 70–80°C for 1–2 min.



**Figure 1.** Sample pretreatment and TXRF measurement procedures.

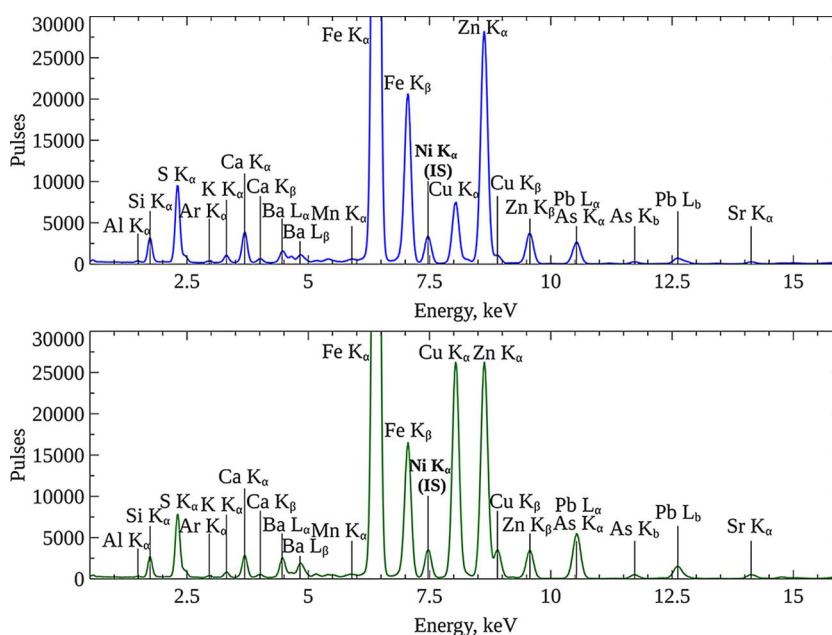
### Optimizing measurement conditions

Suitable masses of the sample and volumes of ethylene glycol for suspension preparation were determined. Increasing the sample mass leads to spectrum distortions due to appearance of pile-up and double energy peaks. Decreasing the sample amount raises the analysis error due to lack of representative sample. As a result, 5–6 mg of finely grounded sample and 1 ml of ethylene glycol were found to be optimal, for suspension preparation. The volume of the suspension transferred to the support was 1  $\mu$ l. Under these conditions, the dead time of energy dispersive detector does not exceed 10%.

Nickel was used as the internal standard. The use of gallium, successfully applied in previous works, had to be abandoned, since it turned out that a loss of gallium occurs when the substrate was heated with the slurry. Selenium, which is also widely used in TXRF, has aspectral line Se  $K\beta$  (12.49 keV) overlapping with Pb  $L\beta$  line (12.61 keV) which is significant for determination of lead because Pb  $L\alpha$  line (10.5 keV) overlaps with As  $L\alpha$  line (10.54 keV) (see Figure 2). Standardless analysis of the available samples showed that nickel in ores is present at undetectable levels. In addition, the closeness of the energy of the Ni  $K\alpha$  (7.47 keV) line to the lines of the most interesting elements Cu  $K\alpha$  (8.04 keV) and Zn  $K\alpha$  (8.62 keV) is shown to be convenient. This promotes the correctness of the determination of these elements.

### TXRF measurements

The measurements were performed with energy-dispersive TXRF spectrometer S2 Picofox (Bruker Nano, Germany). Mo  $K\alpha$  (17.5 keV) radiation is used for X-ray fluorescence excitation. The acquisition time was 500 s. The spectra obtained were processed by Spectra 7 (Bruker Nano) software using optimized Bayes fit technique.



**Figure 2.** Typical TXRF spectra of copper-zinc ore samples: U-1 (top) with the lowest copper concentration and U-5 (bottom) with the highest copper concentration.

## Results and discussion

The concentrations of elements were determined using internal standard quantification:

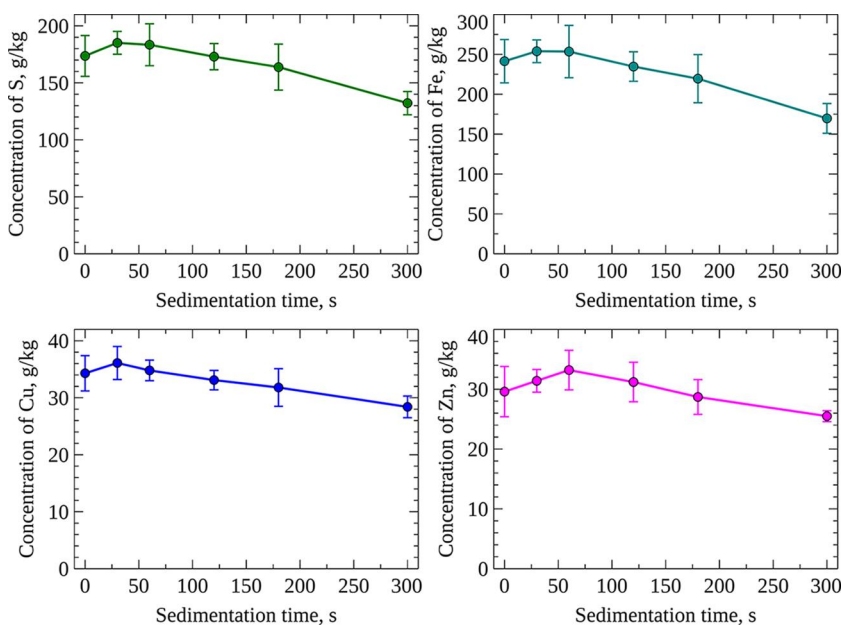
$$C_i = \frac{N_i \cdot C_{IS} \cdot S_{IS}}{S_i \cdot N_{IS}} \quad (1)$$

where  $C_i$  is the elemental concentration.  $N_i$  is the integral intensity of element,  $S_i$  is the sensitivity for the element (determined during spectrometer calibration procedure), and  $C_{IS}$ ,  $N_{IS}$ , and  $S_{IS}$  are the concentration, integral intensity and sensitivity for the internal standard (IS), respectively.

Integral intensity of spectral lines is determined by algorithms in Spectra 7 software. Typical TXRF spectra of copper-zinc ores are shown on Figure 2.

To estimate the stability of the suspensions, one sample was homogenized with shaking and being allowed to stand for a specified period of time; then a drop of the suspension was analyzed by the protocol described above.

Figure 3 shows the concentrations of several elements as a function of sedimentation time. Changes in concentration of different elements are comparable to each other, so it seems to be no different in composition for particles of different sizes. It is seen that 2 min after homogenization the concentration only changes slightly and this change is comparable with the confidence level of determination. At the same time, it takes no more than 30 s to obtain a droplet from homogenized suspension and the concentration does not change during the sampling of a droplet. So it can be inferred that the stability achieved in ethylene glycol is enough for TXRF for this analysis. For samples with higher density values, dispersion media with higher viscosity, e.g., glycerol or glycerol–water mixtures, can be used.



**Figure 3.** Sedimentation curves for major elements in copper-zinc ores suspensions in ethylene glycol.

**Table 1.** Concentration of elements in copper-zinc ores determined by TXRF.

Element	Concentration, g/kg						
	U-1	U-2	U-3	U-4	U-5	U-6	U-7
Al	26 ± 2	20 ± 1.1	22 ± 2	27 ± 1.2	19.3 ± 0.5	20 ± 3	32 ± 4
S	173 ± 14	127 ± 14	176 ± 7	155 ± 13	174 ± 18	198 ± 9	180 ± 20
K	6.2 ± 0.5	5.5 ± 0.2	6.9 ± 0.3	7.3 ± 0.5	5.8 ± 0.5	4.7 ± 0.1	7.4 ± 0.7
Ca	17.8 ± 0.6	13.7 ± 0.7	24.7 ± 0.2	22 ± 2	18.3 ± 1.4	14.1 ± 0.9	28.2 ± 0.9
Mn	0.28 ± 0.02	0.65 ± 0.11	0.24 ± 0.03	0.39 ± 0.07	0.29 ± 0.04	0.27 ± 0.03	0.28 ± 0.03
Fe	240 ± 14	200 ± 20	250 ± 20	210 ± 20	240 ± 30	250 ± 10	230 ± 20
Cu	6.5 ± 0.5	14 ± 1	24 ± 2	33 ± 2	34 ± 3	8.3 ± 0.7	6.7 ± 0.9
Zn	25 ± 2	31 ± 2	18.3 ± 0.8	25 ± 3	30 ± 4	20.5 ± 0.8	21 ± 3
As	1.1 ± 0.2	1.9 ± 0.2	2.3 ± 0.4	2.3 ± 0.3	3.2 ± 0.4	1.7 ± 0.2	1.2 ± 0.3
Rb	0.033 ± 0.004	0.027 ± 0.005	0.028 ± 0.007	0.022 ± 0.004	0.026 ± 0.004	0.034 ± 0.003	0.031 ± 0.008
Sr	0.12 ± 0.01	0.33 ± 0.07	0.22 ± 0.04	0.22 ± 0.01	0.32 ± 0.09	0.07 ± 0.01	0.11 ± 0.03
Ba	17 ± 2	41 ± 4	24 ± 3	23.8 ± 0.7	34 ± 5	8.6 ± 0.9	12.5 ± 1.3
Pb	1.3 ± 0.15	2.4 ± 0.6	2.6 ± 0.5	2.3 ± 0.2	4.0 ± 0.8	1.3 ± 0.15	1.2 ± 0.2

The results of the elemental composition of various ore samples are listed in Table 1. The copper concentration varies between 0.5 and 4 mass% and the zinc concentration varies between 2–3 mass%. All of the ore samples contain high concentrations of iron (20–25 mass%) and sulfur (15–20%, 13% in one of the samples) and can be classified as sulfide ores (FeS<sub>2</sub> matrix) which is the most widespread copper ore (Schlesinger et al. 2011). Usually copper ores contain 0.5–2% of copper. Hence, samples U-4 and U-5 can be classified as relatively rich samples.

The variability between samples is presumably a result of extraction of the ore in different work shifts from different horizons of the mine. The average concentration which can roughly represent the average copper content in the deposit fits this estimation. Also, the samples contain matrix elements (Al, Si, S, K, Ca, Mn, As, Rb, Sr, Ba, Pb). The relative standard deviation of measurements basically does not exceed 10%. Unfortunately, the proposed technique is not able to determine significant elements for copper processing including silver and gold due to spectral interferences (e.g., Ag L $\alpha$  (2.98 keV) with Ar K $\alpha$  (2.96 keV) and Au L $\alpha$  (9.72 keV) with Zn K $\beta$  (9.57 keV)) and the strongly ununiform distribution of these elements.

## Conclusion

A new approach for rapid direct TXRF analysis of solid state samples is proposed. This approach is based on non-aqueous high viscosity liquids as dispersion media for preparation of suspensions. Using high viscosity liquids significantly reduces requirements for sample preparation, e.g., particle size after grinding and the choice of appropriate surfactant for stabilizing the suspension. We have applied the proposed technique for the determination of the elemental composition of copper-zinc ores. We have found that ethylene glycol suspensions are quite stable during the analysis due to the high viscosity. According to this principle, we presume that higher viscosity liquids such as glycerol or glycerol–water mixtures can be used to obtain stable suspension of more dense or inhomogeneous samples.

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