

FEASIBILITY OF TXRF FOR ELEMENTAL ANALYSIS OF FLUID INCLUSIONS IN GALENA CRYSTALS

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Abstract

In the present study the feasibility of total reflection X-ray fluorescence (TXRF) for elemental analysis of individual fluid inclusions (FIs) in galena crystals from the Madan Ore District, Bulgaria was evaluated. Method optimization using a multielement standard and synthetic FIs analogue (Synsol) focused on aliquot volume, dilution, carrier type, and excitation time. Optimal conditions (internal standard Ga with concentration 1 mg L⁻¹; 5 µL aliquots on acrylic carriers; 200–500 s excitation), enabled accurate quantification (±10%) of major FI elements such as K, Ca, Fe, Mn using their K α lines. Among trace elements, Rb and Ba were reliably determined despite their lower sensitivity (L-lines), whereas Cu was systematically underestimated. Zn and Pb were overestimated, most likely as a result of contamination during sampling and sample preparation. At high dilutions, slight underestimation was observed for elements present at lower concentrations in Synsol (e.g., Cu, Rb) and for those quantified using less sensitive L-lines, such as Ba. Light elements were undetectable due to the instrument's limitations. Application to natural FIs confirmed TXRF as a rapid, sensitive, and minimally invasive method for µL-scale fluid inclusion analysis in ore systems, with accuracy influenced on element-specific chemistry and matrix effects.

Key words: fluid inclusions, galena crystals, synthetic fluid inclusions analogue, TXRF analysis

Introduction. Fluid inclusions (FIs) are microscopic volumes of paleofluids trapped in minerals during their growth or later transformation. As relics of the mineral-forming environment they provide valuable insights into ore deposition. Due to their small size and encapsulation, the analysis of FIs requires a combination of microscopic, thermal, chemical, spectroscopic, thermodynamic modelling, and other methods, each with specific abilities and limitations [1–4].

Typically, FIs are aqueous chloride solutions rich in Na, K, and Ca ($\text{Na} > \text{K} > \text{Ca}$). Special attention is paid to ore elements (Fe, Cu, Zn, Pb) and some indicator pairs such as Rb–Cs and Sr–Ba, which help in understanding better the formation and evolution of the ore-forming solutions [5–7]. Although LA-ICP-MS is the preferred technique for single-FI analysis, challenges such as elemental fractionation, calibration difficulties, possible contaminations, and limited reproducibility motivate the search for alternatives [2, 8].

The present study estimates the potential of total reflection X-ray fluorescence (TXRF) for elemental analysis of individual FIs in galena crystals from the Madan Ore District. These μL -scale gas-liquid inclusions, located near crystal surfaces, enable direct piercing, fluid release under gas pressure, and sample collection [9, 10]. TXRF was selected for its high sensitivity, rapid multi-element detection, ability to perform repeatable measurements using an internal standard (IS), and minimal sample consumption, which aligns with the principles of green analytical chemistry [11, 12].

Our approach consisted of two steps: first, optimization of the analytical procedure using a multielement standard and a synthetic FI analogue, followed by analysis of natural inclusion to demonstrate the reliability of TXRF for μL -scale samples.

Experimental. Instrumentation. TXRF analysis was carried out using a benchtop S2 PICOFOX 400 (Bruker Nano GmbH, Germany) with a Mo anode X-ray tube (50 W, 1000 μA max) and a multilayer monochromator (17.5 keV). A silicon drift detector (SDD, 30 mm^2 , < 49 eV) recorded the spectra. Samples were deposited on 30 mm diameter, 3 mm thick fused silica or acrylic glass carriers. Gain correction was performed using As $\text{K}\alpha$ (10.53 keV). The raw data were processed using SPECTRA 7 software. Samples were weighed with a SECURA125-1S semi-micro balance (0.01 mg precision, Sartorius AG). Ultrapure water was produced using an Adrona CB-1903 system (Latvia).

Standard solutions and measurement procedure. A certified ICP multi-element standard solution (Certipur[®], Merck) [13], containing 23 elements including Ga at 1000 mg L^{-1} each in 6.5% HNO_3 , and traceable to SRM[®], was used for method validation and optimization. A 1000-fold dilution in ultrapure water yielded a 1 mg L^{-1} working solution. Aliquots (5 and 10 μL) were deposited on acrylic and silica carriers, dried under an IR lamp, and analyzed at exposure times ranging from 60 to 500 s. Five replicates were prepared for each condition. Element identification and quantification were performed automatically using Ga

(1.00 mg L⁻¹) as an IS.

Data processing. Element identification and quantification were performed automatically using Ga (1.00 mg L⁻¹) as an IS [14,15]. Concentrations (C_i) were calculated using equation (1), based on the ratio of net intensities (N_i/N_{is}) and relative sensitivities (S_i/S_{is}) stored in the software's database. Lower limits of detection (LLD_i) were determined by the 3σ criterion equation (2), and their dependence on exposure time was described by equation (3) [14].

$$(1) \quad C_i = \frac{C_{is} \times N_i \times S_{is}}{N_{is} \times S_i},$$

$$(2) \quad LLD_i = \frac{3 \times C_i \times \sqrt{N_{BG}}}{N_i},$$

$$(3) \quad LLD_i \approx \frac{1}{\sqrt{t}}.$$

Preparation and analysis of a synthetic FI analogue (Synsol). A synthetic analogue solution (Synsol) was prepared to simulate hydrothermal ore-forming brines. The elemental composition and concentrations of this solution were based on data accumulated over a century of FI analyses [16,17]. Analytical-grade reagents and ultrapure water were used. Na, K, and Mn were added as chlorides (pre-dried NaCl and KCl, and MnCl₂·4H₂O); Ca and Li as in situ-prepared chlorides by neutralizing their respective carbonates with HCl; and Rb and Ba as solid nitrates. Trace elements were introduced by Merck Titrisol[®] standards. The final solution was acidified to pH $\approx$ 1 for stability. The composition of the prepared Synsol was as follows (in mg L⁻¹): Na 22.860; K 3.597; Ca 1.711; Li 350; Mn 228; Mg 25.1; Fe 228; Cu 29.6; Zn 57.0; Pb 11.4; Al 57.0; B 228; Rb 29.6; Ba 106. Total salinity (6.84 w/w%) was in good agreement with the experimental value (6.86 w/w%) determined by the dry residue method. For optimization of experimental conditions, various Synsol aliquots (0.5–10 μ L) were diluted to 0.2–1.0 mL and spiked with Ga to a final concentration of 1 mg L⁻¹. After thorough mixing, three 5 μ L aliquots were successively deposited onto acrylic disks, each followed by drying under an IR lamp, and then measured with a 500 s exposure. All samples were prepared and analyzed in triplicate.

Sampling and analysis of a natural FI. A FI was taken from a galena druze collected at the Mogilata deposit (Madan Ore District, Bulgaria). Following the procedure described by BONEV [9] and PIPEROV et al. [10], the depression on the crystal surface indicating the FI was cleaned with acetone, and the thin galena membrane was pierced with a tungsten needle. The released droplet was collected using a pre-weighed silica glass capillary. The inclusion content (0.40 mg $\approx$ 0.40 μ L) was transferred into 0.2 mL ultrapure water and spiked with Ga

to a final concentration of 1 mg L⁻¹. The sample was then treated and analyzed identically to Synsol.

Results and discussion. Optimization of experimental parameters for TXRF analysis. A multielement reference solution was used to optimize analytical parameters across elements of varying atomic number – light ($Z < 14$), medium ($Z \approx 20\text{--}40$), and heavy ($Z > 40$). As the standard solution contained Ga, used as a common IS, no additional spiking was needed. The effects of carrier type (silica vs. acrylic glass), aliquot volume, and excitation time on measurement accuracy and precision were evaluated [15]. Aliquots of 5 μL formed thin, uniform layers fitting within the detector’s effective area (10 mm²), enabling accurate quantification. An excitation time of 60 s was insufficient, while extending it to 1000 s offered no further improvement. Optimal results were obtained at 200 and 500 s. Carrier type had negligible influence. Acrylic disks were preferred due to their low cost and disposability, avoiding the time-consuming and acid-cleaning procedure required for silica glass carriers [16]. To assess deposition variability, five replicates were measured per sample. Results under optimal conditions are presented in Table 1.

Elements with $K\alpha_{1,2}$ lines efficiently excited by Mo $K\alpha_{1,2}$ radiation (17.5 keV) produced strong, well-resolved signals, allowing precise quantification. In contrast, heavy elements like Ba, Tl, Pb, and Bi, detected via low-sensitivity L-lines were quantified with lower accuracy. Light elements (Li, B, Na, Mg, Al) were undetectable due to air absorption [14]. Ag, In, and Cd posed difficulties due to spectral overlap of their $L\alpha_1$ lines with intense Ar and K signals, leading to K overestimation. Manual inclusion of these elements in the peak search enabled proper deconvolution and quantification, correcting the K value and slightly lowering Ca, while other elements remained unaffected. However, due to high measurement uncertainty (RSD 14–33%), TXRF was unsuitable for reliable quantification of Ag, In, and Cd under the examined conditions.

Optimization of TXRF analysis of Synsol solution. FIs typically range from 0.5 to 2 μL and require careful dilution to ensure detectable analyte concentrations without compromising trace quantification. IS concentration must be balanced for accuracy across a wide range. Aliquot volume should be optimized to form thin but sufficiently dense layers to allow accurate trace element detection.

Dilution tests (1:100 to 1:400) showed that no single ratio was universally optimal, but dilutions from 1:100 to 1:250 generally provided the best compromise between accuracy for major elements and trace element quantification (Table 2, Fig. 1). Repeating the pipetting and drying steps three times (5 μL each) yielded consistent results across the tested elements [18].

As expected, light elements (Li, Na, Mg, Al, B) were not detected. The major components of Synsol, K and Ca, as well as the minor constituents Mn and Fe, were quantified within or close to the $\pm 10\%$ range at all dilution levels, which can be attributed to the optimal IS concentration and the high sensitivity of

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Measured concentrations of reference solution (1 mg L^{-1}) using $5 \text{ }\mu\text{L}$ aliquots on acrylic and quartz carriers at 200 and 500 s excitation. Values are mean $\pm$ SD from five replicates; LLDs are also listed

		Acrylic glass discs (200 s)		Acrylic glass discs (500 s)		Silica glass discs (500 s)	
Element & Line		Mean $\pm$ SD (mg L^{-1}) ($n = 5$)	LLD (mg L^{-1})	Mean $\pm$ SD (mg L^{-1}) ($n = 5$)	LLD (mg L^{-1})	Mean $\pm$ SD (mg L^{-1}) ($n = 5$)	LLD (mg L^{-1})
K	$\text{K}\alpha_{1,2}$	1.24 ± 0.03	0.021	1.23 ± 0.02	0.016	1.25 ± 0.02	0.012
K*	$\text{K}\alpha_{1,2}$	0.93 ± 0.07	0.021	0.98 ± 0.05	0.016	0.96 ± 0.08	0.012
Ca	$\text{K}\alpha_{1,2}$	1.10 ± 0.02	0.019	1.08 ± 0.02	0.008	1.14 ± 0.02	0.005
Ca*	$\text{K}\alpha_{1,2}$	1.06 ± 0.06	0.019	1.06 ± 0.04	0.008	1.08 ± 0.07	0.005
Cr	$\text{K}\alpha_{1,2}$	1.08 ± 0.01	0.005	1.07 ± 0.01	0.005	1.08 ± 0.01	0.003
Mn	$\text{K}\alpha_{1,2}$	1.06 ± 0.02	0.004	1.03 ± 0.01	0.004	1.08 ± 0.02	0.003
Fe	$\text{K}\alpha_{1,2}$	1.13 ± 0.03	0.004	1.09 ± 0.02	0.003	1.06 ± 0.02	0.002
Co	$\text{K}\alpha_{1,2}$	1.04 ± 0.02	0.003	1.03 ± 0.01	0.003	1.06 ± 0.01	0.002
Ni	$\text{K}\alpha_{1,2}$	1.06 ± 0.01	0.002	1.02 ± 0.01	0.001	1.05 ± 0.01	0.001
Cu	$\text{K}\alpha_{1,2}$	1.09 ± 0.02	0.002	1.06 ± 0.02	0.002	1.10 ± 0.02	0.001
Zn	$\text{K}\alpha_{1,2}$	1.07 ± 0.03	0.002	1.05 ± 0.03	0.002	1.09 ± 0.02	0.001
Ga	$\text{K}\alpha_{1,2}$	IS of 1.00 mg L^{-1}					
Sr	$\text{K}\alpha_{1,2}$	0.97 ± 0.03	0.004	1.02 ± 0.03	0.003	0.96 ± 0.01	0.002
Ba	$\text{L}\alpha_1$	0.79 ± 0.03	0.016	0.80 ± 0.02	0.010	0.75 ± 0.03	0.007
Tl	$\text{L}\alpha_1$	0.82 ± 0.03	0.004	0.83 ± 0.03	0.003	0.82 ± 0.02	0.002
Pb	$\text{L}\alpha_1$	0.84 ± 0.08	0.002	0.94 ± 0.07	0.002	0.84 ± 0.05	0.002
Bi	$\text{L}\alpha_1$	0.74 ± 0.04	0.002	0.74 ± 0.04	0.002	0.71 ± 0.04	0.001
Ag*	$\text{L}\alpha_1$	1.5 ± 0.5	0.12	1.4 ± 0.3	0.096	1.2 ± 0.3	0.084
In*	$\text{L}\alpha_1$	0.8 ± 0.2	0.046	0.8 ± 0.2	0.034	1.0 ± 0.2	0.026
Cd*	$\text{L}\alpha_1$	1.0 ± 0.2	0.061	0.9 ± 0.2	0.045	0.7 ± 0.1	0.039

Elements without asterisks were automatically quantified by the software. Ag, In, and Cd (marked with asterisks) were manually added for peak search, which led to recalculated concentrations of K and Ca (with asterisk); other elements remained unaffected. LLD values represent the average from five measurements.

their $\text{K}\alpha$ lines. Trace elements exhibited more variable behaviour. Rb remained within $\pm 10\%$ at all dilutions despite its low concentration ($\sim 30 \text{ mg L}^{-1}$) and detection via an L-line, whereas Cu, at a comparable level and measured by a sensitive $\text{K}\alpha$ line, was systematically underestimated with increasing dilution. This discrepancy suggests that Cu losses may be related to the formation of Cu–Cl complexes in the Synsol solution, which could affect crystallization and the uniformity of deposition on the sample carrier [19]. Matrix effects driven by Zn–Cl complexation may partly explain the observed overestimation of Zn, but

T a b l e 2

Elemental concentrations in Synsol (prepared vs. measured at Syn-1 to Syn-4) and in a natural fluid inclusion. Results are given as mean $\pm$ SD from triplicate analyses

Sample	K	Ca	Mn	Fe	Cu	Zn	Rb	Ba	Pb
Synsol prepared mg L ⁻¹	3 597	1 711	228	228	29.6	57	29.6	106	11.4
Syn-1	10 μ L Synsol : 1000 μ L H ₂ O (dilution 1:100)								
Mean $\pm$ SD, (mg L ⁻¹)	3 850 $\pm$ 62	1 780 $\pm$ 32	239 $\pm$ 5	233 $\pm$ 5	26.6 $\pm$ 1.5	113 $\pm$ 5	34 $\pm$ 2	108 $\pm$ 5	16 $\pm$ 1
RSD (%)	1.6	1.8	2.1	2.3	5.6	4.7	6.3	4.3	9.0
Syn-2	2 μ L Synsol : 500 μ L H ₂ O (dilution 1:250)								
Mean $\pm$ SD, (mg L ⁻¹)	3 420 $\pm$ 37	1707 $\pm$ 41	241 $\pm$ 4	247 $\pm$ 8	26.2 $\pm$ 1.6	131 $\pm$ 7	30.3 $\pm$ 2.4	109 $\pm$ 6	27 $\pm$ 2
RSD (%)	1.1	1.6	1.7	3.1	6.7	5.3	7.8	5.1	7.5
Syn-3	1.0 μ L Synsol :200 μ L H ₂ O (dilution 1:200)								
Mean $\pm$ SD, (mg L ⁻¹)	3 272 $\pm$ 35	1 619 $\pm$ 31	259 $\pm$ 10	253 $\pm$ 6	23.3 $\pm$ 0.7	124 $\pm$ 2	28 $\pm$ 2	89 $\pm$ 2	30 $\pm$ 4
RSD (%)	1.1	1.9	3.6	2.5	3.0	1.2	8.5	2.0	12.1
Syn-4	0.5 μ L Synsol : 200 μ L H ₂ O (dilution 1:400)								
Mean $\pm$ SD, (mg L ⁻¹)	3 015 $\pm$ 35	1 673 $\pm$ 22	221 $\pm$ 13	227 $\pm$ 17	21 $\pm$ 1	137 $\pm$ 6	27 $\pm$ 2	87 $\pm$ 5	27 $\pm$ 3
RSD (%)	1.2	1.3	5.8	7.3	5.8	4.4	6.7	5.3	11.7
Fluid inclusion	0.40 mg : 200 μ L H ₂ O (dilution 1:500)								
	K	Ca	Mn	Fe	Cu	Zn	Rb	Ba	Sr
Mean $\pm$ SD (mg L ⁻¹), <i>n</i> = 3	3 430 $\pm$ 62	3 653 $\pm$ 88	10.2 $\pm$ 0.6	74 $\pm$ 1	28.3 $\pm$ 0.9	41.7 $\pm$ 0.9	63 $\pm$ 3	37 $\pm$ 1	72 $\pm$ 2
RSD (%)	1.8	2.4	6.1	1.7	3.1	2.4	4.7	2.9	3.4

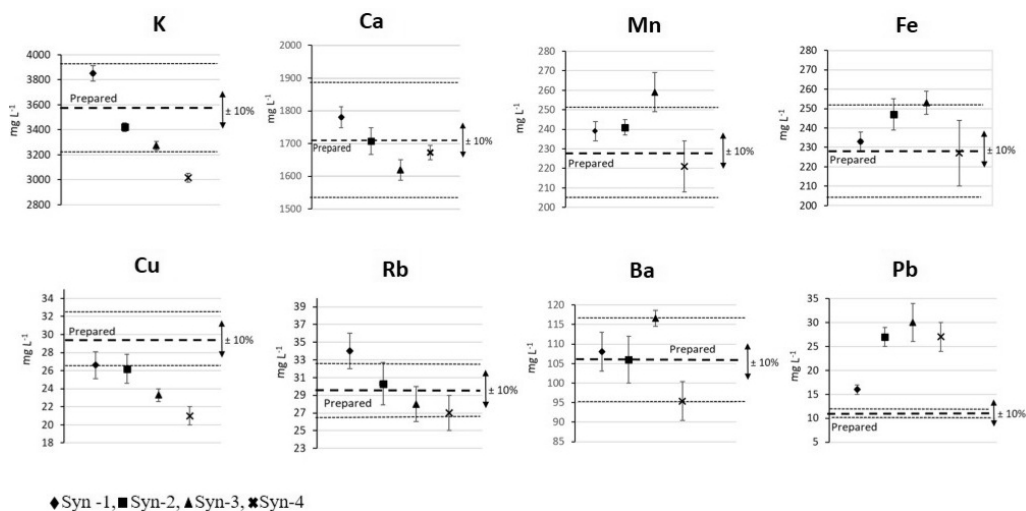


Fig. 1. Comparison between prepared and measured concentrations of elements in Synsol at four dilution levels (Syn-1 to Syn-4). Error bars represent RSD from replicate analyses. The dashed horizontal line marks the prepared concentration, and dotted lines indicate the $\pm 10\%$ deviation range

the magnitude of the deviation ($> 100\%$) strongly suggests contamination during sample preparation [20]. Ba, like Rb, does not form complexes and remains within $\pm 10\%$ despite being quantified via the less sensitive L-line. Pb is consistently overestimated, most probably due to contamination from the galena host during sampling.

Overall, these results highlight that TXRF accuracy is not governed solely by line sensitivity and analyte concentration, but also by element-specific chemistry, matrix effects, and sample preparation.

Analysis of natural fluid inclusion. The composition of the fluid inclusion extracted from the galena crystal reveals a distinct enrichment in Ca, Rb, and Sr compared to the synthetic reference solution, as well as significantly lower concentrations of Fe and Mn. These differences, including the occurrence of Sr, are not unexpected since fluid inclusion chemistry commonly varies between deposits. The obtained results will be further analyzed to elucidate the geochemical processes that have driven the evolution of this region.

Conclusions. The present study demonstrates that TXRF is a suitable method for μL -scale elemental analysis of μL -sized FI in galena. The optimized procedure ensures accurate quantification of key elements such as K, Ca, Fe, and Mn. Trace elements Rb and Ba also showed good agreement with the prepared values, despite being quantified through less sensitive L-lines. In contrast, Cu was systematically underestimated, most likely due to Cu-Cl complexation and deposition effects. Analysis of a natural FI confirmed that reliable multi-element information can be obtained even from a single inclusion. Minimal sample con-

sumption, low detection limits, and the ability to repeat measurements on the same inclusion make TXRF a practical and cost-effective alternative for FI analysis in ore-related studies.

REFERENCES

- [1] RANDIVE K. R., K. R. HARI, M. L. DORA et al. (2014) Study of fluid inclusions: methods, techniques and applications, *Gond. Geol. Mag.*, **29**(1–2), 19–28.
- [2] LIN X., W. GUO, L. JIN, S. HU (2020) Review: Elemental analysis of individual fluid inclusions by laser ablation-ICP-MS, *At. Spectrosc.*, **41**(1), 1–10.
- [3] LADENBURGER S., B. F. WALTER, M. A. W. MARKS, G. MARKL (2020) Combining ion chromatography and total reflection X-ray fluorescence for detection of major, minor and trace elements in quartz-hosted fluid inclusions, *J. Anal. Chem.*, **75**(11), 1477–1485.
- [4] LIU Y., T. WAGNER, T. FUSSWINKEL (2024) An integrated approach for quantifying fluid inclusion data combining microthermometry, LA-ICP-MS, and thermodynamic modeling, *Chem. Geol.*, **644**, 121863.
- [5] BODNAR R. J., P. LECUMBERRI-SANCHEZ, D. MONCADA, M. STEELE-MACINNIS (2014) Fluid inclusions in hydrothermal ore deposits. In book: *Treatise on Geochemistry*, 2nd Edition, Oxford, Elsevier, 119–142.
- [6] LARGE S. J. E., E. BAKKER, P. WEIS et al. (2016) Trace elements in fluid inclusions of sediment-hosted gold deposits indicate a magmatic-hydrothermal origin of the Carlin ore trend, *Geology*, **44**(12), 1015–1018.
- [7] ZUO X., C. LI, J. ZHANG et al. (2020) Geochemical characteristics and depositional environment of the Shahejie Formation in the Binnan Oilfield, China, *J. Geophys. Eng.*, **17**(3), 539–551.
- [8] BORISOVA A., S. SALVI, G. VELASQUEZ et al. (2021) Quantification of major and trace elements in fluid inclusions and gas bubbles by laser ablation inductively coupled plasma mass spectrometry (LA-ICP-MS) with no internal standard: a new method, *Eur. J. Mineral.*, **33**(3), 305–314.
- [9] BONEV I. K. (1977) Primary fluid inclusions in galena crystals. 1. Morphology and origin, *Mineral. Deposita (Berl.)*, **12**(1), 64–76.
- [10] PIPEROV N. B., N. P. PENCHEV, I. K. BONEV (1977) Primary fluid inclusions in galena crystals. 2. Chemical composition of the liquid and gas phase, *Mineral. Deposita (Berl.)*, **12**, 77–89.
- [11] SCHMELING M. (2019) Total reflection X-ray fluorescence, *Phys. Sci. Rev.*, **4**(7), 1–23.
- [12] IVANOVA E. H., A. K. DETCHEVA (2012) Green analytical chemistry and its perspectives in Bulgaria, *Bulg. Chem. Commun.*, **44**(1) 5–10.
- [13] Certipur[®] Certified reference material (Merck KGaA, Frankfurter Str. 250, 64293 Darmstadt, Germany), Ord. N 1.11355.0100, Lot N HC60659055.
- [14] Bruker Nano GmbH (2017) S2 Picofox user manual.
- [15] PASHKOVA G. V., A. G. REVENKO (2015) A review of application of total reflection X-ray fluorescence spectrometry to water analysis, *Appl. Spectrosc. Rev.*, **50**, 443–472.

- [16] ROEDDER E. (1972) Composition of fluid inclusions, US Geol. Surv., Prof. Pap. 440 JJ, 163 pp, <https://doi.org/10.3133/pp440JJ>.
- [17] KOTZEVA, B. G., M. GUILLONG, E. STEFANOVA, N. B. PIPEROV (2011) LA-ICP-MS analysis of single fluid inclusions in a quartz crystal (Madan ore district, Bulgaria), J. Geochem. Explor., **108**(3), 163–175.
- [18] GEORGIEVA R., A. DETCHEVA, M. KARADJOV et al. (2013) Total reflection X-ray fluorescence analysis of trace elements in Bulgarian bottled mineral waters of low and high mineral content, Int. J. Environ. Anal. Chem., **93**(10), 1043–1051.
- [19] COLLINGS M. D., D. M. SHERMAN, K. V. RAGNARSDOTTIR (2000) Complexation of Cu²⁺ in oxidized NaCl brines from 25 °C to 175 °C: results from in situ EXAFS spectroscopy, Chem. Geol., **167**(1), 65–73.
- [20] MEI Y., D. M. SHERMAN, W. LIU et al. (2015) Zinc complexation in chloride-rich hydrothermal fluids (25–600 °C): A thermodynamic model derived from ab initio molecular dynamics, Geochim. et Cosmochim. Acta, **150**, 265–284.

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