



Calibration of Portable XRF Spectrometer in Sn-W Ore-Bearing Granites: Application in the Cínovec Deposit (Erzgebirge/Krušné Hory Mts., Czech Republic)

Ilja KNĚSL¹⁾, Tereza JANDOVÁ²⁾, Petr RAMBOUSEK³⁾, Karel BREITER⁴⁾

¹⁾ Ing.; Czech Geological Survey, Geologická 6, 152 00 Praha 5, Czech Republic

²⁾ Mgr.; Czech Geological Survey, Geologická 6, 152 00 Praha 5, Czech Republic

³⁾ RNDr.; Czech Geological Survey, Geologická 6, 152 00 Praha 5, Czech Republic

⁴⁾ RNDr., Ph.D.; Institute of Geology AS CR, Rozvojová 269, 165 00 Praha 6, Czech Republic

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Abstract

This study evaluates the suitability of portable X-Ray fluorescence spectrometry (PXRF) in the environment of granites and greisens with Sn-W and secondary mineralization of other important elements (Rb, Y, La, Ce, Nb, Ta and Tl). International certificated reference materials (CRM), historical data from the sixties based on the borehole CS-1, current analyses in accredited laboratory and data measured by a portable X-ray fluorescence spectrometer (PXRF) with factory settings were evaluated in this study. Powder CRMs and samples from borehole CS-1 were analysed by PXRF. The results of PXRF analysis were then tested for reliability, credibility, accuracy and precision. The accuracy was calculated as a relative percent difference (RPD), regression equations and correlation coefficients. A detailed statistical evaluation of the results proves, that PXRF can be a very useful method for a primary determination of main, secondary and trace elements. Comparison of the conventional methods and the PXRF shows a good correlation of different analytical methods and a good possibility of using the PXRF method for a future selection of samples for subsequent more demanding and expensive conventional and special analyses. A calibration of the PXRF spectrometer to the lithological environment of Sn-W ore-bearing granites and greisens was made by the statistical comparison of the methods.

Keywords: PXRF analyzer, comparison of methods

Introduction

Currently is increasing use of portable X-ray fluorescence (PXRF) technology as a routine tool for data collection in mine and exploration settings. Studies several authors demonstrate a diverse range of applications of PXRF data including resolving stratigraphic complexity [1], prediction of mineralogy and metallurgical performance at a deposit-scale [2], studies of elements associated with Au mineralization [3], and exploration targeting for Ni-sulphide systems [4]. These PXRF case studies demonstrate that, with careful sampling and analytical protocols, a large geochemical dataset can be produced rapidly and at low cost. In this paper we present a case study which utilises PXRF data collected on granites and greisens environments with Sn-W mineralisation, to better understand their geochemistry. The PXRF data were compared with conventional chemical methods. In the study, the authors have carried out of an experiment to apply user calibration and correction factors to PXRF for better approximation of the measured values to the real concentrations which provide conventional laboratory methods.

About 1600 m deep borehole CS-1 was realized in the centre of the cupola in sixties of the last century [5]. The borehole CS-1 was previously studied by several other authors (e.g. [6,7]).

Methods

Studied materials

Three international CRMs (GnA – greisen; TRV - ore of rare earth elements and ZW-C – zinnwaldite), five internal standards (E1 – granite; E34 – Sn-W ore Cínovec South I; E35 – Sn-W ore Cínovec South I; E36 – Sn-W ore, Krásno and E37 – Sn-W ore, Krupka) and 14 samples from historical borehole CS-1 from greisenized granite body (3 samples of granites, 4 samples altered granites, 3 samples feldspatites, 3 zinnwaldite-granites samples and one sample of greisen) were used for calibration of the PXRF. Elemental concentrations in these international CRMs were taken from [8]. The samples were selected to cover a broad range of compositions in each of the groups, especially for trace elements and metals. Total of 171 samples from the borehole CS-1 (104 granites samples, 43 samples of zinnwaldite-granites, 9 samples of the altered granites, 9 samples of feldspatites and 6 samples of greisens) were measured to test the calibration. All samples were homogenized by standard preparation, firstly crushed in a jaw crusher, then quartered and milled in agate mills for analytical fineness (grain > 0.063 mm).

PXRF

Measurements were performed by spectrometer Delta Premium 50 (Olympus Innov-X Systems, USA), where is installed the mode Light matrix for measurement of geological samples (using three different beams with different intensity: 50 kV, 40 kV and 15 kV, measured reliably lower concentration with an upper limit of 10%). Overview of elements measured in the mode Light matrix is shown in Table 1.

The measurement time of each beam was 120 seconds. During the measuring the head was firmly fixed in the spectrometer measuring table. The instrument was standardized to outer metal standard supplied by the manufacturer before the measurement. The excitation source of the apparatus uses a built-in X-ray tube with Ag-anode at a voltage of 10–50 kV, current 5–50 μ A and six internal filters. Si PiN diode detector is embedded to capture ionizing radiation.

Conventional chemical analysis

Basic analytical work was carried out in the laboratories of Bureau Veritas (former ACMELabs) in Vancouver. Each sample was distributed twice. Multi-acid decomposition with HF (pseudototal decomposition) was carried out to the samples, which were subsequently analysed by ICP-MS for Ti. For analysis of the elements Rb, Y, Nb, Sn, La, Ce, Ta and W, the samples were melted with LiBO_2 , dissolved in acid solution (HCl) and subsequently analysed by ICP-MS.

Accuracy

Measurement accuracy (RPD) was evaluated based on the comparison of the certified values with the values measured by PXRF [9]:

$$RPD = \frac{V_c - V_{XRF}}{V_c} \times 100$$

where *RPD* is relative percent difference, V_c is the CRM value and V_{XRF} is the mean of the PXRF measurement value.

Positive values of RPD indicate lower measured concentrations than the real ones, negative values indicate higher measured concentrations than the real ones. XRF spectrometer measurement accuracy was evaluated according to [9] for each studied element as follows: excellent result $|RPD| < 10\%$, good result $10\% < |RPD| < 25\%$, fair result $25\% < |RPD| < 50\%$ and poor result $50\% < |RPD|$.

Calibration

22 samples, which were measured in the laboratory of the Bureau Veritas (former ACMELabs) in Vancouver, were measured for the correctness of re-

sults. These samples were used as a geo-referenced material. They were measured by the PXRF each sample 30 times and the means of the measurements were plotted to graphs together with the results from Bureau Veritas's laboratory measurements. From these graphs, were calculated trendline equation (Fig. 1). Correction factor for each element was calculated using following equation:

$$y = a * x + b$$

where: *a* – slope of the trendline; *b* – intersection with the Y axis.

The calculated correction factors were exchanged in the factory settings.

Testing of the calibration

A total of 171 samples from the borehole CS-1 were first measured by PXRF with the factory settings and then with calculated correction factors for the individual elements. The results of both measurements were compared with the measurement of ICP-MS (Bureau Veritas, Fig. 2).

Results

The measured concentrations for each element according to the PXRF were plotted against the Bureau Veritas (ICP-MS) concentrations, and compared to a 1:1 line to evaluate how well the original values were reproduced. Results for CRMs and selected rock samples are presented in Figure 1 and results for a whole set of samples from CS-1 are showed in Figure 2. Table 2 shows the results of calculation of the RPD from measurements of the CRMs and measurements of selected 14 samples from the borehole CS-1. Figure 3 shows the example of analysis of samples from the borehole CS-1 of greisen deposit Cínovec very good reproducibility of the results PXRF (with factory settings and with settings of the correction factors) with conventional method (ICP-MS).

Discussion and conclusions

The best results by measurements without correction factor (Tab. 2) were reached for Ti ($|RPD| < 10\%$), Rb ($|RPD| < 15\%$), Sn, W, La ($|RPD| < 25\%$) and Nb ($|RPD| < 50\%$). RPD for other studied elements (Y, Ce and Ta) was worse than 50%. When compared with the real samples, RPD values were slightly better (Tab. 2). Using the correction factor resulted in significant improvement for some elements (Rb and Nb).

The accuracy of the results depends on the matrix of the studied material, as well as on the analytical methods in the conventional laboratory. To verify the

Tab. 1. List of elements measured in various modes

Tab. 1. Wykaz pierwiastków mierzonych różnymi metodami

Mode	Beam	Measured elements
Light matrix	#1 (50 kV)	U, Sr, Y, Zr, Th, Nb, Mo, Rh, Pd, Ag, Cd, In, Sn, Sb, Ba, La, Ce, Pr, Nd
	#2 (40 kV)	Fe, Co, Ni, Cu, Zn, Hf, Ta, W, Hg, As, Pt, Se, Au, Tl, Pb, Bi, Rb
	#3 (15 kV)	P, S, Cl, K, Ca, Ti, V, Cr, Mn

Tab. 2. Minimum, maximum RPD values calculated from CRMs and average RPD values from selected samples from CS-1 for studied elements

Tab. 2. Minimum, maksimum wartości RPD wyliczonej z CRM i średniej wartości RPD dla wybranych próbek z CS-1

Element	Measurement of CRMs without correction factor		Measurement of CRMs with correction factor		Measurement of selected samples from CS-1 without correction factor	Measurement of selected samples from CS-1 with correction factor
	RPD Min (%)	RPD Max (%)	RPD Min (%)	RPD Max (%)	Average value (%)	Average value (%)
Sn	-2.439	19.254	-5.158	17.615	-1.872	-48.251
W	-21.625	-21.625	-19.688	-19.688	2.418	4.824
Rb	-12.805	-9.718	-1.337	-0.082	-5.535	-0.328
Y	52.831	52.831	52.646	52.646	23.839	8.951
La	-22.051	-22.051			-56.813	
Ce	49.395	77.743	63.506	63.506	6.753	15.472
Nb	-40.284	-24.209	-6.170	12.626	-34.453	-4.186
Ta	-140.805	-9.919	-68.966	13.415	-83.511	-33.000
Tl	8.167	8.167	8.824	8.824	18.845	2.991

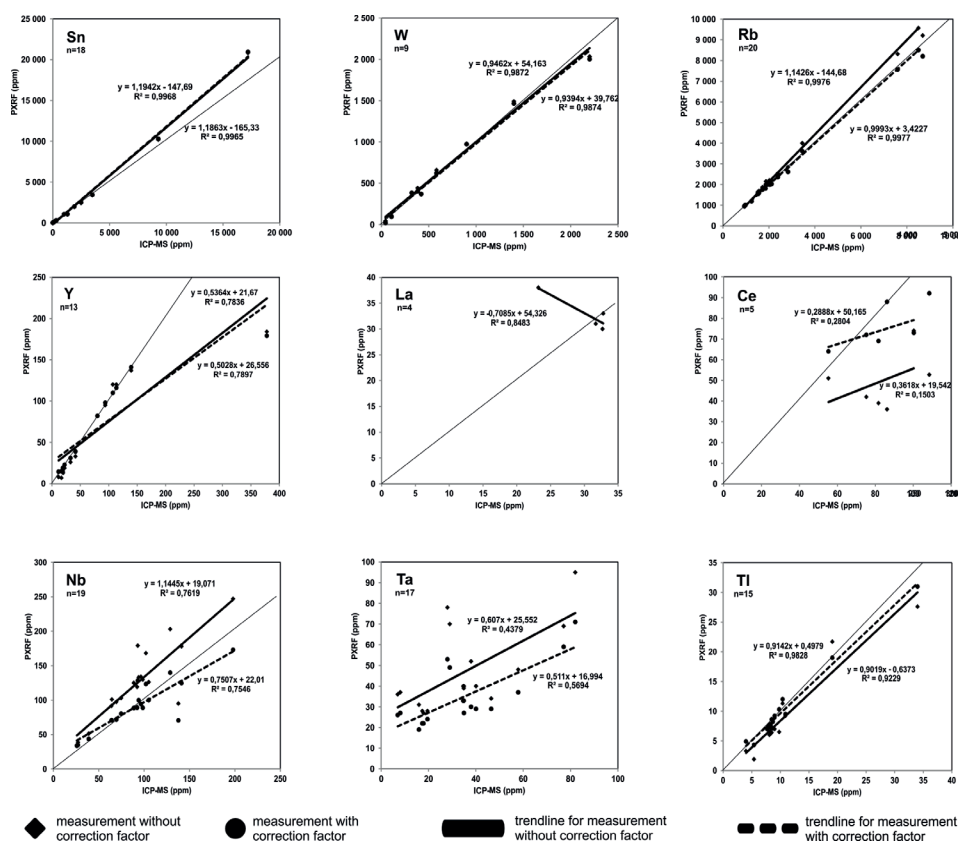


Fig. 1. Comparison of the PXRf-measurements with the certified values and results of the conventional method in the accredited laboratories (ICP-MS: Bureau Veritas Vancouver)

Rys. 1. Porównanie pomiarów PXRf z wartością uzyskaną w akredytowanych laboratoriach (ICP-MS: Bureau Veritas Vancouver)

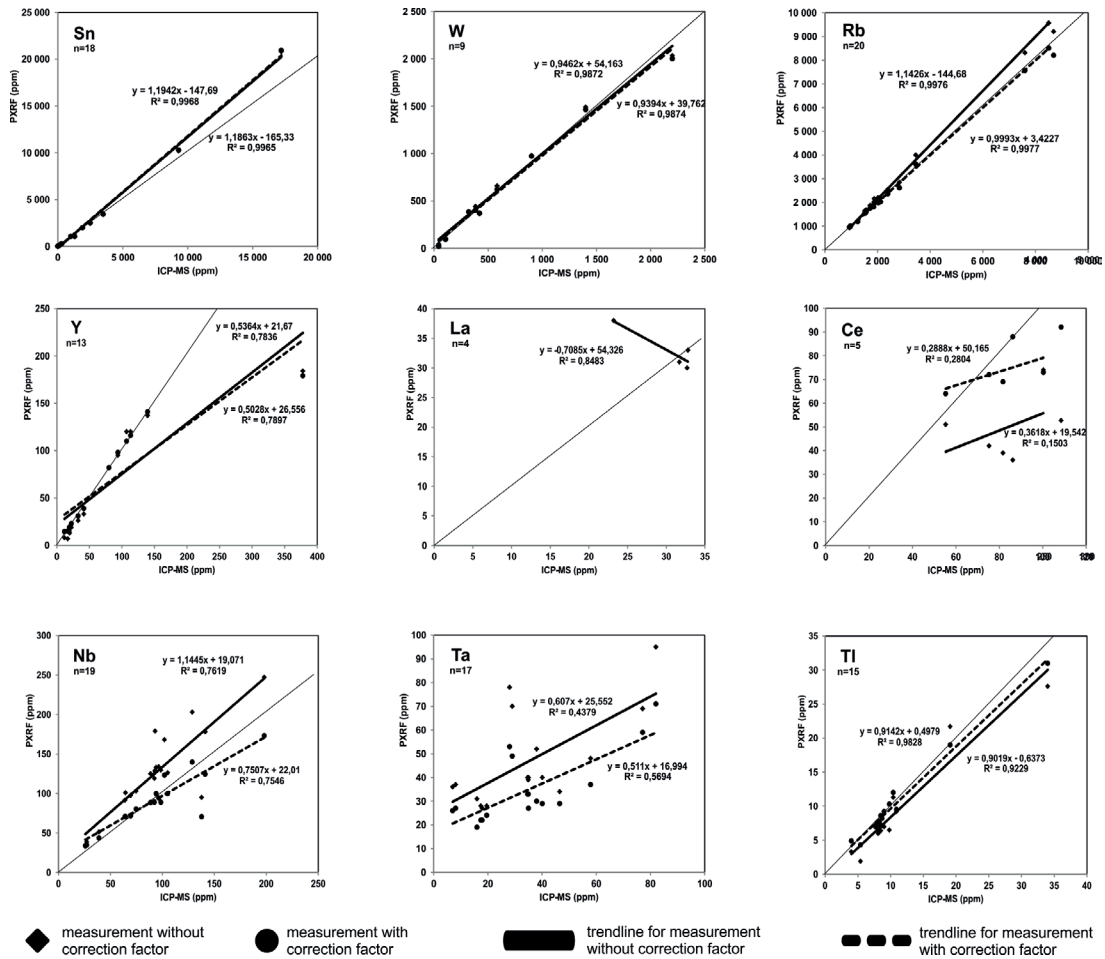


Fig. 2. Comparison of the PXRF-measurements with the results of the conventional method in the accredited laboratories (ICP-MS: Bureau Veritas Vancouver)

Rys. 2. Porównanie pomiarów PXRF z wartością uzyskaną w akredytowanych laboratoriach (ICP-MS: Bureau Veritas Vancouver)

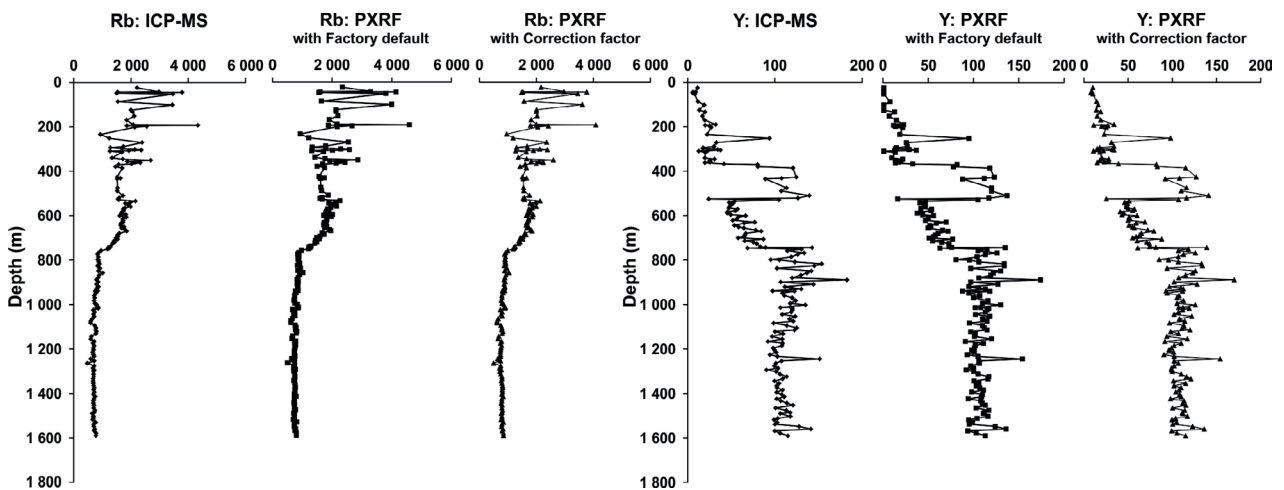


Fig. 3. Example of the use of the PXRF method for the analysis of pulp samples from the drill core of the borehole CS-1 and its comparison with the conventional method made by accredited laboratories (ICP-MS: Bureau Veritas Vancouver): Rb and Y

Rys. 3. Przykład wykorzystania metody PXRF do analizy próbek z odwiertu CS-1 i porównanie z wynikami z akredytowanego laboratorium (ICP-MS: Bureau Veritas Vancouver): Rb and Y

reliability of the measurements, a comparison with commonly used and proven laboratory methods (ICP, AAS) was used in number of works. Statistical evaluation of samples prepared for measurement with portable XRF made for example [10]. Other authors [11,12] discussed rapid verification of a wider range of trace elements in the various types of geological materials by portable XRF spectrometer. Comparison of results of portable XRF spectrometer with FAAS method was done by [13] and comparison of portable XRF spectrometry with ICP-OES method tested [14]. Both the major and trace elements studied and measured by PXRF [15], and calculated the average RPD in the range from 3 to 31.2% in basalts and rhyolites. Three CRMs were compared by [16] with PXRF data for selected elements. They calculated [16] the RPD values for elements which we study too, as follows: La (9 and 279%), Ce (2 and 163%), Y (17%), Nb (31, 34 and 41%), Rb (43 and 48%), Zr (25 and 71%), Mo (4 and 34%) and W (435 and 718%). In our study are showed excellent results (according to [9]) of the PXRF measurements in comparison with the CRM values for elements such as Tl, and for real samples Sn, W, Rb and Ce. The elements W, Rb and La show good results in comparison with CRM, for real samples it concerns elements Y and Tl.

The PXRF is an effective method for determining the geochemical characteristics of the envi-

ronment and it is possible to use it for example for surface screening of the source of mineralization. Data from PXRF correlate well with conventional chemical analyses. Modern PXRF spectrometers achieve ppm level for a wide range of elements, including major, basic elements, some special metals, some LREE as well as some precious metals. Wide range of detectable elements makes this tool useful in exploration for many types of ore. The example from greisen deposit Cinovec showed a very good reproducibility of results compared to real results. It could serve for selection of samples, which would be analysed by more expensive conventional analytical methods. Calculation of the correction factor for some elements shifted the results closer to the real values, but it was not always the case. The calculation is time consuming and the outcome is not corresponding to the effort. It is better to use the calculated RPD values of the international CRMs.

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Literatura – References

1. GAZLEY, M.F.; VRY, J.K.; DU PLESSIS, E.; HANDLER, M.R. 2011. "Application of hand-held X-ray fluorescence analyses to metabasalt stratigraphy, Plutonic Gold Mine, Western Australia." *Journal of Geochemical Exploration* 110: 74–80.
2. GAZLEY, M.F.; DUCLAUX, G.; FISHER, L.A.; DE BEER, S.; SMITH, P.; TAYLOR, M.; SWANSON, R.; HOUGH, R.M.; CLEVERLEY, J.S. 2012. "3D visualisation of portable X-ray fluorescence data to improve geological understanding and predict metallurgical performance at Plutonic Gold Mine, Western Australia." *Applied Earth Science Trans.* 120: 88–96.
3. FISHER, L.A.; GAZLEY, M.F.; BAENSCH, A.; BARNES, S.J.; CLEVERLEY, J.; DUCLAUX, G. 2014. "Resolution of geochemical and lithostratigraphic complexity: A workflow for application of portable X-ray fluorescence to mineral exploration." *Geochemistry: Exploration, Environment, Analysis* 14: 149-159.
4. LE VAILLANT, M.; BARNES, S.J.; FISHER, L.; FIORENTINI, M.L.; CARUSO, S. 2014. "Use and calibration of portable X-ray fluorescence analysers: Application to lithochemical exploration for komatiite-hosted nickel sulphide deposits." *Geochemistry: Exploration, Environment Analysis* 14: 199–209.

5. ŠTEMPROK, M.; ŠULCEK, Z. 1969. "Geochemical profile through an ore-bearing lithium granite." *Economic Geology* 64: 392–404.
6. RUB, A.K.; ŠTEMPROK, M.; RUB, M.G. 1998. "Tantalum mineralization in the apical part of the Cinovec (Zinnwald) granite stock." *Mineralogy and Petrology* 63: 199–222.
7. JOHAN, Z.; JOHAN, V. 2005. "Accessory minerals of the Cí'novec (Zinnwald) granite cupola, Czech Republic: indicators of petrogenetic evolution." *Mineralogy and Petrology* 83: 113–150.
8. 1994. "Govindaraju. Compilation of working values and sample description for 383 geostandards." *Geostandard Newsletter* 18: 1–158.
9. U.S. EPA. XRF technologies for measuring trace elements in soil and sediment. Niton XLt 700 Series XRF Analyzer. Innovative technology verification report EPA/540/R-06/004. Wasington, 2006.
10. BERNICK, MB.; GETTY, D; PRINCE, G.; SPRENGER, M. 1995. "Statistical evaluation of field-portable X-ray fluorescence soil preparation methods." *Journal of Hazardous Materials* 43: 111–116.
11. HEWITT, A.D. 1995. "Rapid screening of metals using portable high resolution X-ray fluorescence spectrometers." Available online: <http://www.crrel.usace.army.mil/techpub/CRREL_Reports/reports/SR95_14.pdf>.
12. KALNICKY, JD.; SINGHVI, R. 2001. "Field portable XRF analysis of environmental samples." *Journal of Hazardous Materials* 83: 93–122.
13. MÄKINEN, E.; KORHONEN, M.; VISKARI, EL.; HAAPAMÄKI, S.; JÄRVINEN, M.; LU, L. 2005. Comparison of XRF and FAAS methods in analysing CCA contaminated soils. *Water, Air, and Soil Pollution* 171: 95–110.
14. KILBRIDE, C.; POOLE, J.; HUTCHINGS, T.R. 2006. "A comparison of Cu, Pb, As, Cd, Zn, Fe, Ni and Mn determined by acid extraction/ICP–OES and ex situ field portable X-ray fluorescence analyses." *Environmental Pollution* 143: 16–23.
15. CERNUSCHI, F.; FORD, M.T.; BOSCHMANN, D.; DILLES, J.H.; CONREY, R.M. 2013. "Test of a user defined calibration in a portable XRF for litho geochemistry applications." in: E. Jonsson et al (eds.) "Mineral deposit research for high-tech world. Proceedings of the 12th Biennial SGA Meeting" *Geological Survey of Sweden* 1: 180–183.
16. SIMANDL, G.J.; STONE, R.S.; PARADIS, S.; FAJBER, R.; REID, H.M.; GRATAN, K. 2014. "An assessment of a handheld X-ray fluorescence instrument for use in exploration and development with an emphasis on REEs and related specialty metals." *Mineralium Deposita* 49: 999–1012.

Kalibracja przenośnego spektrometru fluorescencji rentgenowskiej (XRF) na granitach zawierających Sn-W ze złoża Cínovec (Erzgebirge / Krušné Hory Mts., Republika Czeska)

Niniejsze badania sprawdzają przydatność przenośnego spektrometru fluorescencji rentgenowskiej (ang. skrót PXRF) w warunkach występowania granitów i grejzenów z Sn-W oraz wtórnej mineralizacji innych pierwiastków (Rb, Y, La, Ce, Nb, Ta i Tl). W badaniach uwzględniono międzynarodowe certyfikowane materiały odniesienia (ang. skrót CRM), dane historyczne z lat 60 oparte na odwiertach CS-1, bieżące analizy w akredytowanych laboratoriach i dane uzyskane z przenośnego spektrometru fluorescencji rentgenowskiej (PXRF) z ustawieniami fabrycznymi. CRM proszkowe oraz próbki pobrane z odwiertu CS-1 przeanalizowano w PXRF. Wyniki analizy PXRF zostały następnie poddane testom na niezawodność, wiarygodność, dokładność i precyzję. Dokładność została policzona jako względna różnica procentowa (RPD), równania regresyjne i współczynniki korelacji. Szczegółowa ocena statystyczna wyników dowodzi, że PXRF może być pomocną metodą we wstępnym określaniu zawartości pierwiastków głównych, wtórnych i śladowych. Porównanie metod konwencjonalnych z metodą PXRF pokazało pozytywną korelację różnych metod analitycznych i możliwość stosowania metody PXRF do przyszłych doborów próbek w celu dalszych trudniejszych i droższych analiz konwencjonalnych i specjalistycznych. Kalibracja spektrometru PXRF do warunków występowania litu w granitach i grejzenach zawierających rudę Sn-W została sporządzona na podstawie statystycznego porównania wymienionych metod.

Słowa kluczowe: przenośny analizator XRF, porównanie metod