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Application of field-portable XRF on Coltan: factory calibration or user calibration?

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Abstract

Field-portable x-ray fluorescence (FPXRF) has many applications in the earth and environmental sciences including coltan (columbite-tantalite) exploration, mining and trading. Common elements of interest including Ta, Nb, Sn, W and Fe can be easily identified and quantified using FPXRF. All of these elements show good correlation between FPXRF and lab values in the analyzed known samples. The factory calibration provides acceptable and accurate results up to a certain concentration for most of these elements (3% Ta, 16% Sn, 2% W, and 2% Fe). However, for Nb, two user calibrations (below and above 11% Nb) are required to obtain accurate result.

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1. Introduction

Tantalum (Ta) and niobium (Nb) as two relatively rare metals (8 ppm Nb and 0.7 ppm Ta in the continental crust; Rudnick and Gao, 2004) are mainly found as oxides in nature. Coltan is referred to the combination of columbite [(Fe,Mn)Nb₂O₆] and tantalite [(Fe,Mn)Ta₂O₆] which are the common ore minerals of Nb and Ta, respectively. These minerals are genetically associated with geochemically distinct granitoids and pegmatites which are enriched in some rare elements such as Li, F, Rb, Cs, Be, Nb, Ta, REE, Sn, W, U, Th, Zr and Y. Weathering of such rocks and deposits and transportation of weathered particles form placer deposits which can be found in the ancient and modern stream sediments. In such deposits, coltan may be associated with cassiterite (SnO₂) and wolframite [(Mn, Fe)WO₄].

Field-portable x-ray fluorescence (FPXRF) is a technique that has gained momentum and application in various fields from geology/mineralogy to mining (grass root exploration to exploitation and ore grade control), environmental science, metallurgy, geo-archeology and even oil/gas exploration and production (e.g. Arne et al., 2014; Cheng, 2014; Conrey et al., 2014; Gazley et al., 2014; Le Vaillant et al., 2014; Lemièrre et al., 2014; Quiniou and Laperche, 2014; Simandl et al., 2014; Yuan et al., 2014; Balaram 2017, 2019). This technique can produce fast and accurate results (depending on the concentration, sample type and operational conditions) with little or no sample preparation. FPXRF offers on-site real time analysis that makes it a

suitable method during green root and brown field exploration such as drill management, identification of anomalies, preparation of geochemical maps in real time, and selecting proper samples for laboratory analysis.

XRF is a mature and known technology for several decades. FPXRF can simultaneously analyze a wide range of elements from Mg to U with detection limits down to a few ppm for some elements. These devices host this capability in a small handheld pistol package (~1.3 kg) or portable desktop version (~14 kg) (Fig. 1). XRF is a surface analysis technique in which x-ray penetration inside the surface of most samples is mostly minimal (<0.1 mm). In this technique, the sample is bombarded with high-energy primary x-rays or gammas, although most manufacturers recently use x-ray tubes. The excited atoms in the sample emit characteristic "secondary" (or fluorescent) x-rays, which are detected, plotted and calculated based on energy and intensity. The energy of a detected secondary x-ray is unique for each element, and the corresponding intensities are converted to concentrations and reported as percent (%) or part per million (ppm).

One of the common issues in using FPXRF for many applications is the reliability of factory calibration. The common questions include: are the produced data reliable and accurate? Is it possible to improve accuracy of FPXRF data? In this paper, application of this analytical technique on coltan and associated metals (Ta, Nb, Sn, W and Fe) is explained in details. In addition, suitability of the factory calibration on these metals and benefits of a user calibration will be discussed.

2. Material and methods

Dry powder specimens of 21 previously analyzed (by Inductively Coupled Plasma Mass Spectrometry, ICP-MS) samples were analyzed in 32 mm sample cups fitted with polypropylene film. The analyses were carried out using a ThermoFisher Niton XL3t-950 with x-ray excitation at 50 kV, 200 μ A, using Ag anode. The instrument utilizes a 45 mm² Silicon Drift Detector (SDD) and the operation was performed using a 229 mm adjustable touchscreen on the instrument. The analyzer offers 3 modes which can be selected based on sample type and matrix: Mining Mode, Soil Mode, TestAll Geo. In this research, the Mining Mode was selected which collected spectra in all 4 filters (Fig. 2): Main, Low, High, Light (60 seconds analysis time in each filter). A particular set of elements were analyzed in each of the 4 filters. The Mining Mode mode utilizes fundamental parameters and relies on the detector response to pure element spectra. The Mining Mode offers 2 factory calibrations CuZn (used for common applications) and TaHf (for coltan and associated minerals). The latter is a special mode where the performance of the analyzer is enhanced by eliminating elements with X-ray energies close to Nb and Ta. The energy values (in kilo electron volt, Kev) for K α , K β , L α , and L β lines are respectively 16.61, 18.62, 2.17, 2.26 for Nb and 57.52, 65.21, 8.15, 9.34 for Ta. Available elements are identified using the collected spectra. Using the TaHf factory calibration, the peak intensities from each spectrum are used to calculate elements concentrations after applying corrections. The interested elements can be chosen to show as elements or oxides (e.g. Fe₂O₃,

Nb₂O₅, etc.). These raw data are compared with the lab data of the same samples to evaluate reliability and accuracy. The correlation of raw values and lab data is a good indicator of the performance of the FPXRF. If both data sets show good correlation, the accuracy of the raw FPXRF data can be improved by defining and applying a user calibration. This calibration uses the equation of the best fit in the X-Y graph of raw data vs lab values to adjust the raw values and yield a final data.

3. Results

Trading value and mineralogy of the coltan and its associated minerals show that Nb, Ta, Sn, W, and Fe are the most important metals. Therefore, the assay results of these elements are discussed here.

3.1. Sn concentration

Tin concentration in the analyzed samples ranges widely from 0.01 to 74.09% (Table 1). In terms of consistency, the portable XRF data show very good correlation with the lab data (Fig. 3a). In addition, FPXRF data are very close to the lab data in samples with up to 16% Sn (Table 1); this means that the factory calibration is suitable for such samples. However, based on the factory calibration, the FPXRF values are lower in samples with >16% Sn concentrations. To increase accuracy of such samples, user calibration is required. To construct a user calibration, a graph is made for samples with >16% Sn (Fig. 3b) and then the equation for the best fit line is used to calculate a new values based on the raw FPXRF values (Table 1). It is notable that these new post-calibrated FPXRF values are closer to the lab values.

3.2. Nb concentration

Niobium concentration ranges from 0.10 to 41.40% in the samples analyzed by lab (Table 2). Although the FPXRF values show a good correlation with the lab data (Fig. 4a), it is notable that all raw FPXRF values are lower than the lab assays. This suggests that the factory calibration is not suitable for accurate quantification, and indicates that a user calibration is required. As samples with lab values of Nb>18% (~11% in FPXRF) show a well-defined trend line (Fig. 4a), two sets of calibration curves are made and applied to the raw FPXRF values: one for a set of samples with FPXRF values of Nb>11%, and another for a set of samples with FPXRF values of Nb<11% (Figs. 4b and 4c). Using this method, the accuracy of data is improved significantly (Table 2).

3.3. Ta concentration

Similar to Sn and Nb, the lab values of Ta show a wide range from 0.07 to 50.37% (Table 3). Overall, the lab and FPXRF data show good correlation (Fig. 5a). For some unknown reason, FPXRF data are abnormally high in three samples (406, 106, 46); as a result, these samples are off the best fit line.

Comparison of FPXRF data with lab values shows that the factory calibration is only suitable for samples with low Ta concentration (Ta<3%); for samples with higher Ta, a user calibration (Fig. 5b) is used to increase accuracy of FPXRF data (bold numbers in Table 3). The three erroneous samples are excluded in the user calibration adjustment.

3.4. W concentration

Most analyzed samples have lab assays of $W < 2\%$ and only one sample has $W > 40\%$. The FPXRF data in the low W samples show high correlation with lab assays (Figs. 6a and b). It appears that the factory calibration is suitable for the low W samples and delivers acceptable accurate results, although the accuracy can be improved slightly using a user calibration (*italic numbers in Table 4*).

In one sample, the lab value for W is 40.78%, whereas the FPXRF value is higher (46.35%). As there is only one high W sample, the best fit based on all of the analyzed samples is used to improve accuracy of FPXRF for this sample. Using this method, the calculated FPXRF value of W for this sample is 40.76% (Table 4).

Table 4. Range of W concentration in the analyzed coltan samples. *Italic numbers are post-calibrated for samples with $W < 2\%$. The bold number is based on the best fit using all samples.*

Sample	W (pXRF)		W-Lab
	Raw	Final	
12	0.00	<i>0.02</i>	0.00
83	0.00	<i>0.02</i>	0.00
84	0.00	<i>0.02</i>	0.00
87	0.00	<i>0.02</i>	0.00
88	0.00	<i>0.02</i>	0.00
194	0.00	<i>0.02</i>	0.02
243	0.00	<i>0.02</i>	0.04
301	0.00	<i>0.02</i>	0.06
25	0.00	<i>0.02</i>	0.00
165	0.09	<i>0.09</i>	0.02
167	0.10	<i>0.10</i>	0.02
175	0.16	<i>0.14</i>	0.00
47	0.18	<i>0.16</i>	0.22
46	0.26	<i>0.21</i>	0.30
Belfer 9	0.37	<i>0.30</i>	0.32
44	0.40	<i>0.32</i>	0.39
406	0.45	<i>0.35</i>	0.43
11	0.50	<i>0.39</i>	0.42
174	1.83	<i>1.38</i>	1.50
106	2.21	<i>1.66</i>	1.51
24	46.35	40.76	40.78

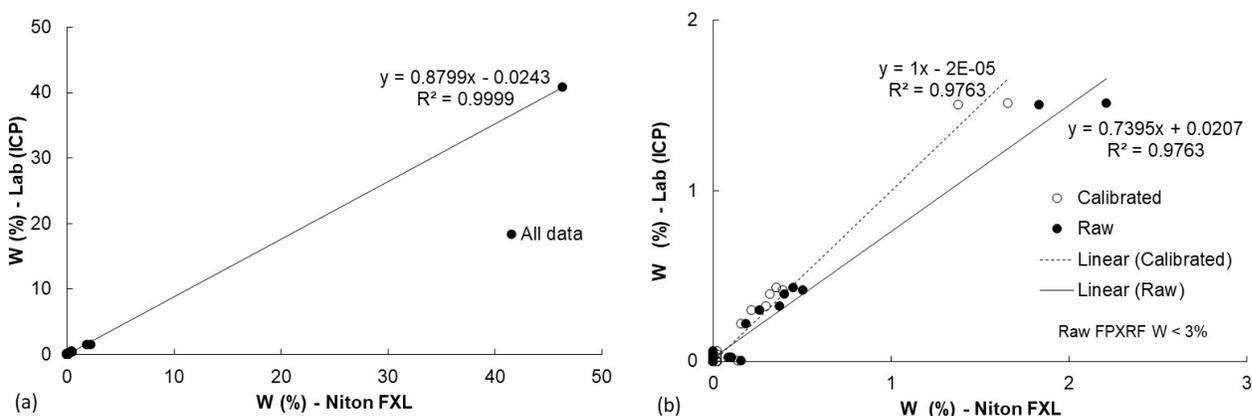


Fig. 6. a) High correlation between raw FPXRF and lab values of W. b) User calibration for samples with raw FPXRF values of $W < 3\%$.

3.5. Fe concentration

Iron concentration in the analyzed samples ranges from 0.06 to 18.82% (Table 5). Comparison of the FPXRF data with lab assays shows a good correlation between these two sets of data (Fig. 7a). It appears that at low concentrations ($< 2\%$ Fe) factory calibrated FPXRF delivers accurate results, however at higher concentrations ($> 2\%$ Fe), a user calibration (Fig. 7b) is required to increase the accuracy of FPXRF data (bold numbers in Table 5).

Table 5. Iron concentration in the analyzed coltan samples. All numbers are based on the factory calibration except the bold numbers which are post-calibrated for samples with $Fe > 2\%$.

Sample	Fe (pXRF)		Fe-Lab
	Raw	Final	
175	0.20	0.20	0.06
194	0.26	0.26	0.37
243	1.07	1.07	1.15
301	1.71	1.71	1.87
87	2.28	3.25	3.50
12	2.33	3.30	2.60
25	2.51	3.46	2.71
88	2.90	3.82	4.39
84	3.53	4.39	3.75
174	5.10	5.82	5.43
167	6.19	6.82	7.16
83	7.01	7.56	8.65
11	7.65	8.15	8.97
165	9.66	9.97	9.09
46	10.20	10.47	10.62
106	10.24	10.50	10.32
24	11.63	11.77	14.07

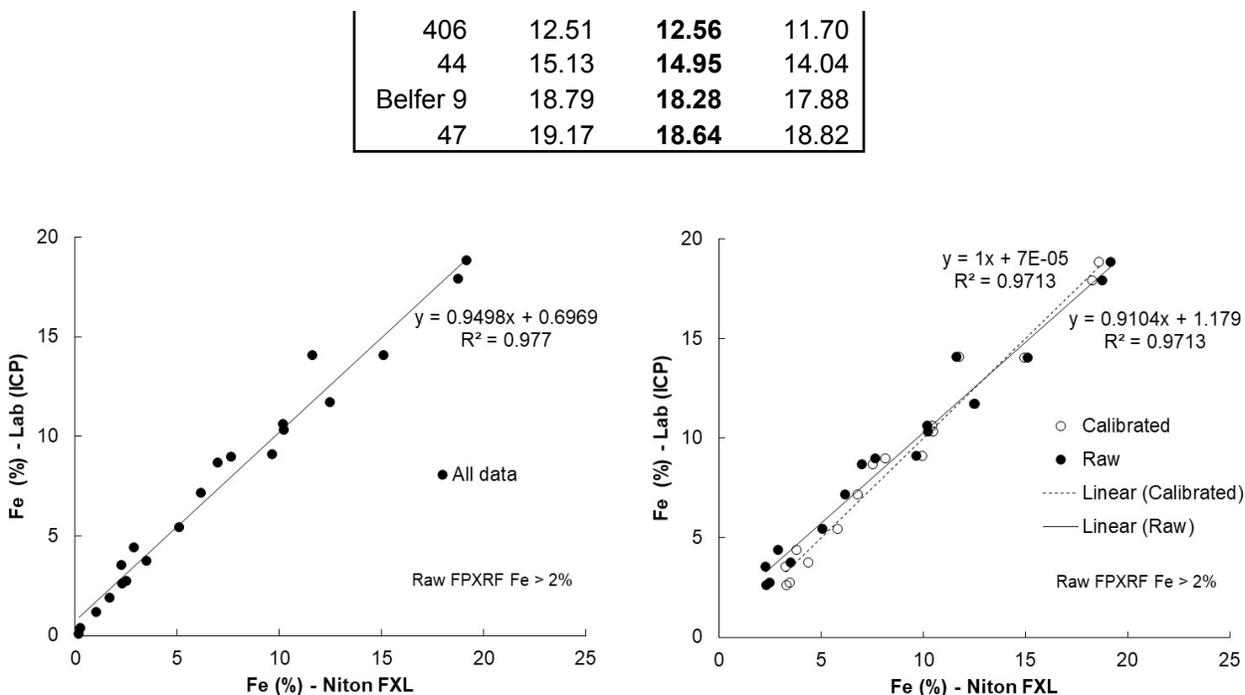


Fig. 7. a) High correlation between raw FPXRF and lab values of Fe. b) User calibration for samples with raw FPXRF values of Fe>2%.

4. Discussion

Several thousands of FPXRF instruments from various manufactures are used in the mining industry. It is proven that this technique is very beneficial to any project; however, the users need to be familiar with limits of the instrument and adjust their expectations accordingly. Although the instrument can provide real time assay data, its capabilities should not be over- or underestimated. The comprehensive Camiro study (Hall et al., 2014) showed that in many cases in order to use FPXRF as a quantitative tool, a user calibration is required. This is mainly due to matrix effect reflecting the fact that the matrix of the user samples may be different from the matrix of the samples used in the factory calibration. As a result, depending on criteria such as sample type, element concentration, and element type, data from each FPXRF instrument may need to be adjusted if high accuracy is required. This adjustment, called user calibration, is done using certified standards or known samples which have been analyzed by laboratory techniques. This research is an example of how the accuracy of raw FPXRF data can be improved applying the user calibration. It shows that for coltan samples, the threshold for the acceptable results (based on the factory calibration) varies depending on the element of interest (Table 6). For example, for samples with Sn<16%, the factory calibration provides accurate results; for higher concentrations (Sn>16%), a user calibration is required. For Ta and Fe, the acceptable threshold is 3% and 2% respectively. Factory calibration provides accurate results for W<2%, but at higher concentrations (40%?), the user calibration is required. For Nb, factory calibration is not suitable

and two user calibrations for Nb<11% and Nb>11% are needed to yield reliable and accurate results.

Table 6. Threshold of acceptable values for the factory and user calibrations.

	Sn	Nb	Ta	W	Fe
Factory calibration	<16%	-	<3%	<2%	<2%
User calibration 1	>16%	<11%	>3%	>40? %	>2%
User calibration 2	-	>11%			

Comparison of the findings from this research with those from the Camiro project (Hall et al., 2014) suggests that similar investigation is needed to identify the acceptable threshold for elements of interest in any FPXRF instrument. This may apply to instruments even from the same manufacturer as technical features, calibration method and quantification calculations and algorithm may vary amongst manufactures and instruments.

5. Conclusions

Field-portable XRF can provide real time assay data on any type of samples in the field or remote labs. However, performance of any FPXRF analyzer should be tested and evaluated before using it on unknown samples. Factory calibration may provide reliable and accurate data on some elements or concentrations. As long as the produced FPXRF data show a good correlation with the lab assays, the former can be adjusted. To increase accuracy of FPXRF data on some elements or concentrations, user calibration can be applied using certified samples or pre-analyzed samples from the same project area. This procedure should be repeated if the sample type, matrix and metal concentration change.

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