

# Hand-held X-ray fluorescence (hXRF) measurements as a useful tool in the environmental and mining sector – Comparative measurements and effects of water content

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**Abstract** In this article, direct hXRF measurements on zinc-, arsenic- and lead-containing tailing material, which has been investigated with regard to its potential for re-mining, will be presented. Measurements on the original moist field material will be compared to measurements on dry material. In general, the evaluation of the hXRF data for the tailing material shows a good relative replication of the element contents determined (chemical analysis). This was not compulsory for such a heterogeneous material. In humid sediments, however, there are considerably large fluctuations in the element concentration.

**Key words** hand-held X-ray fluorescence spectrometer, hXRF, water content influence, tailings

## Introduction

There are various applications of a hand-held XRF analyzer in fields related to mining, in the remediation sector and for environmental hazard analysis. In our research group, an hXRF device has been tested over the last 5 years in a variety of applications. During its application, the following materials were investigated: massive ore bodies, sediments and tailing material, but also composite materials and brown coal.

From the physical background of the XRF measuring principle, it is known that in addition to matrix and grain size effects the water content has a great influence on the results of XRF analysis (Kalnicky 2001). This has already been shown comparing field values with laboratory values (Ussath 2015). The question is, how big is this effect and is it possible to correct the field-measured values?

For re-mining projects of old tailings and environmental assessment, the reliability of the quantification of valuable elements with field methods such as hXRF is important. Studies were carried out on various Chilean tailing materials. Some selected results of these investigations on material of a zinc-gold mine and a copper mine are presented.

## Methods

### X-ray fluorescence analysis and recalibration of raw data

The X-ray fluorescence (XRF) spectrometer is an instrument used for non-destructive detection of major elements and selected trace elements during the investigation of rocks, ores and soils. A hand-held X-ray fluorescence (hXRF) analyzer allows operating on-site for immediate analysis.

For this study, an hXRF Niton XL3t980 analyzer equipped with an Ag-Anode 50 kV X-ray tube and Silicon-Drift-Detector 8 mm spot was used.

For major and trace elements, device-specific correction equations for the measurement of homogenized and dried samples were determined by measuring certified reference materials (CRM). Therefor 21 silicon-based standards, filled in cups and covered with 4  $\mu\text{m}$  polypropylene film (cp. fig. 3, right) were measured with device specific mode *Mining/Mineral*. hXRF output values (raw data) plotted against the certified values shown a defined deviation from the certified values. So the line equation of the trend line was used for deriving a correction equation (Grimmer 2015). Values named *raw* used in this article are not corrected output data, values named *recal* are corrected values using the equation in table 1.

**Table 1** Correction equation, range of recalibration and number of CRM used for the calculation of the correction equation listed for the elements represented in the article.

element	As	Cd	Cu	Mo	Pb
Correction equation	$y = (x-158)/0.638$	$y = x/1.047$	$y = x/0.815$	$y = x/0.919$	$y = (x-24)/0.895$
Recalibration range [ppm]	0 – 7000	500 – 5000	0 – 10000	0 – 35	0 – 10000
Number of CRM used for calculal.	11	2 (not sufficient)	11	7	12

x ... hXRF output value in ppm; y ... recalibrated value in ppm

Usually, even more CRM should be used for the calculation of the correction equation, but currently we do not have so many CRMs with relevant element contents available. The recalibration range (tab. 1) is defined by the highest and lowest element content of the CRMs. So a higher number of CRMs would also expand the recalibration range.

### Comparative hXRF measurements – field and laboratory

Investigations have been carried out by direct hXRF measurements on two different Chilean tailing materials (from a zinc-gold mine and a copper mine), which has been investigated with regard to its potential for re-mining and seepage water problems. Subsequently, the tailing material samples were dried, homogenized and measured again by hXRF. In addition, a complete chemical digestion was done by a commercial laboratory. Samples were digested using sodium peroxide fusion and analyzed for the major and trace elements by ICPMS (FUS-MS-Na<sub>2</sub>O<sub>2</sub>). Results of chemical analysis were compared to the hXRF measurements on the original moist material and on the dry material.

### Influence of water saturation

Water saturation tests were carried out on different tailing materials. For this purpose, the material was saturated in a controlled manner and subsequently dried step by step. After each drying step, hXRF measurements were performed (three hXRF measurements per drying step). Results are presented for the < 20  $\mu\text{m}$  fraction of tailing material of a zinc-gold mine.

## Results and discussion

### Comparative hXRF measurements – Environmentally relevant results

In the following section results for measurements on zinc-gold mine tailing material for arsenic and lead as well as for cadmium and copper are presented. Results are shown in fig. 1 and 2.

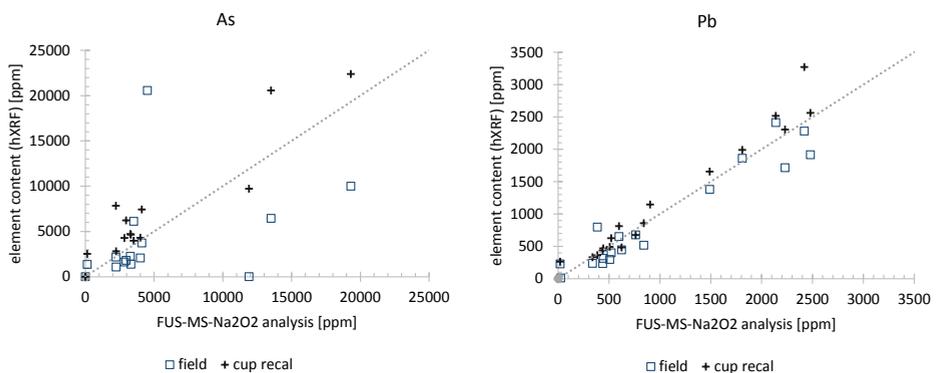
The data series *field* describes the direct measurement on the tailing site or the laboratory measurement of the field-wet state. For the field measurements, raw data of the hXRF measurements are plotted. In general, redundant measurements would be necessary for every sampling point. However, here only one measurement was carried out and later a sample was taken. Due to the variety of areas to be measured, no multiple measurements were possible for reasons of time. After the hXRF field measurement, mixed samples of 0.5 – 1 kg were taken. So the data series *cup recal* describes the results of these mixed, homogenized, dried samples.

The dotted lines in the diagrams (fig. 1 and 2) represents the congruency of element concentrations determined by chemical analysis and values determined by hXRF measurements.

### Arsenic and lead

As shown in fig. 1 left, the majority of samples contains arsenic in a range of 2000 to 5000 ppm, on some cases up to more than 20.000 ppm (2 % As). The recalibration range for arsenic is available up to 7000 ppm. For low As concentrations (< 1000 ppm), the measurement is more reliable. Some samples show a large deviation from the chemical-analytical value – besides, most of the hXRF field measurements show an underestimation. In comparison, the dried, cup-measured and recalibrated values tend to be overestimated.

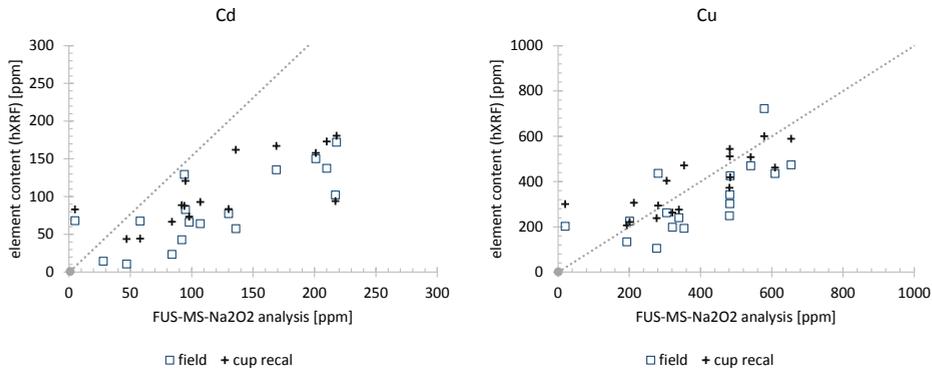
For lead (fig. 1 right), the recalibration equation is applicable up to about 10.000 ppm. The measured values are in the range of 500 to 3000 ppm. Even the raw data show a good correlation to the chemical-analytical values. A clear convergence to the chemical-analytical value is obtained by the recalibration (crosses in fig. 1 right are on the dotted line).



**Figure 1** Comparative hXRF measurements: field-, cup- and chemical-analytical values – As and Pb content in zinc-gold mine tailing material (dotted line: congruency of chemical-analytical value and hXRF value)

## Cadmium and copper

For cadmium and copper, a relatively wide scatter is shown for the field values (fig. 2). The cup-measured and recalibrated samples clearly converge the chemical-analytical value.



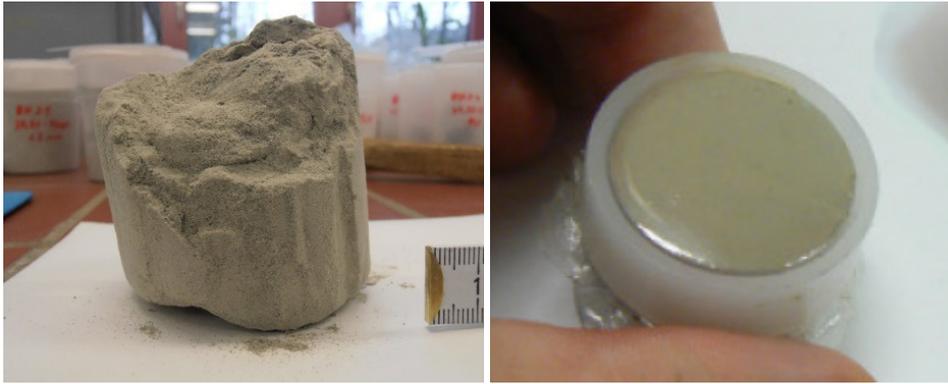
**Figure 2** Comparative hXRF measurements: field-, cup- and chemical-analytical values – Cd and Cu content in zinc-gold mine tailing material (dotted line: congruency of chemical-analytical value and hXRF value)

Interim conclusion: for environmentally relevant elements such as arsenic, cadmium, copper and lead, a magnitude can be indicated with XRF measurements already in the field. However, this measurement is not sufficient for the estimation of the contamination potential – at least sampling is required for an hXRF measurement in the laboratory. In this manner, the detection of lead (in the example up to 3000 ppm) and copper (in the example up to 1000 ppm) is sufficiently reliable for this methodology.

### Comparative hXRF measurements – Mining-relevant results

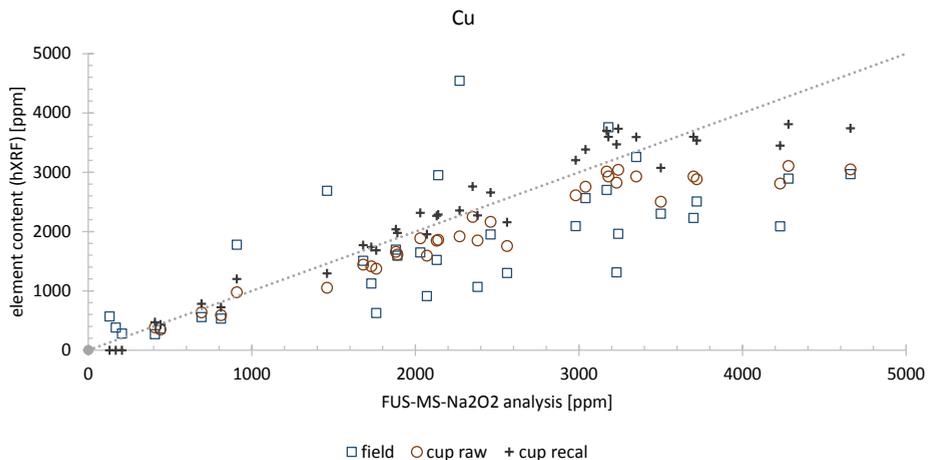
In the focus of the following evaluation is the detection of recoverable elements in old tailing materials using the examples of copper and molybdenum (Mo rather small contents) as well as arsenic (rather under the environmental aspect). As already mentioned in Ussath (2015) the re-mining of certain old tailings bodies in Chile is necessary from a geotechnical safety perspective. Also known is the high copper content in the tailings. For the design of a selective re-mining project, a reliable knowledge of the element respectively copper distribution is required.

Analogously to the already described procedure (diagrams above, fig. 1 and 2), the following section describes the results of measurements on tailing material originating from a porphyry copper-molybdenum deposit. The material comes from drilling cores and represents the various depths of the tailing body. For 37 samples, chemical analysis were performed and compared with hXRF values (see fig. 4). In addition to *cup recal*, there is also a data set *cup raw*, which contains the raw data of the cup measurements before the recalibration (i.e. direct output from the hXRF).



**Figure 3** left: drill core sample; right: cup with dried, homogenized tailing material

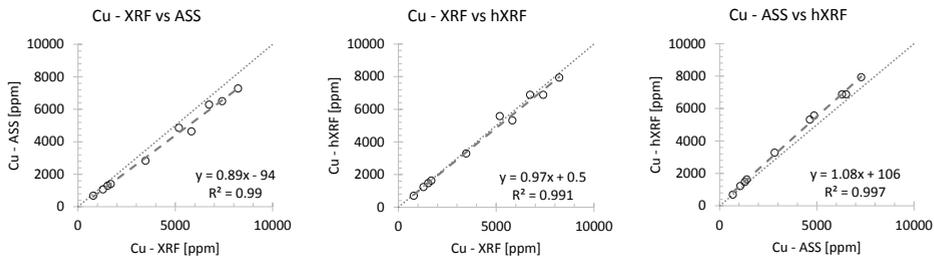
hXRF measurements were made directly on drill core material (fig. 3) in the laboratory. The *field* data set is characterized by spreading and partly high deviations. In general, the cup-measured values (fig. 4) show a better accuracy. However, the hXRF values of the data set *cup raw* tend to underestimate the copper content compared to the chemical-analytical values. After recalibration (*cup recal*), the values are on the “desired dotted line” – that means, for copper content determination a recalibration of the data is reasonable. For a field method, one obtains sufficiently accurate values for the estimation of the resource potential.



**Figure 4** Comparative hXRF measurements: field-, cup- and chemical-analytical values – Cu content in copper mine tailing material (dotted line: congruency of chemical-analytical value and hXRF value)

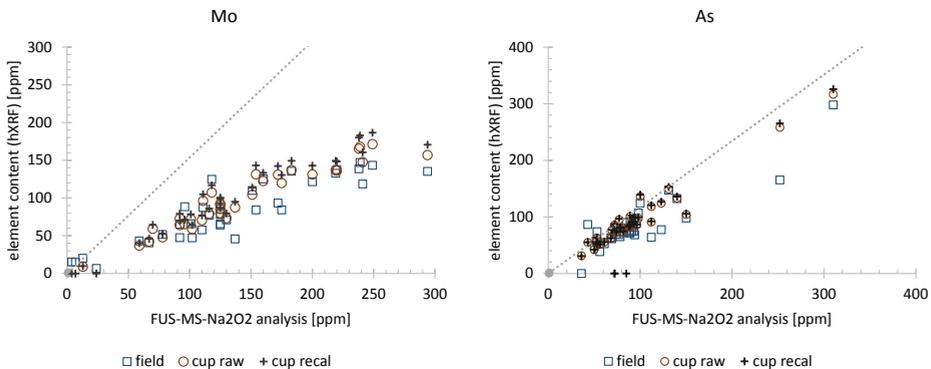
Results from measurements on press tablets (tailing material from the same location) show again good results for copper detection. Press tablets for measurements with an ordinary XRF were measured with hXRF. There was also a review with atomic absorption spectroscopy (AAS). Fig. 5 (left) represents the comparison of the ordinary XRF and the AAS re-

sults at contents smaller than 8000 ppm copper. The XRF shows values slightly higher than AAS measured values. Fig. 5 (center and right) represents the respective comparison of the hXRF with XRF and AAS measurements. There is a very good congruency between hXRF- and XRF-measured values. But also the congruency to the AAS-measured values is considerable, although there is a slight overestimation of the hXRF values compared to the AAS values.



**Figure 5** Comparative hXRF measurements on press tablets: XRF and AAS values – Cu content in copper mine tailing material (dashed line: regression line; dotted line: congruency)

The molybdenum contents in this tailing material are not particularly high, but the general behavior can be shown (fig. 6 left). For molybdenum, our current (hXRF) recalibration range is only up to about 35 ppm. The contents in the tailing material range up to approx. 300 ppm. Despite recalibration and the associated improvement of the data, for molybdenum a clear underestimation by hXRF is remaining. Fig. 6 right shows the arsenic content of the drill core samples. In general, there is a slight dispersion of the *field* values. The difference between *cup raw* and *cup recal* values is insignificant. Nevertheless, a slight improvement compared to the *field* values is obvious.

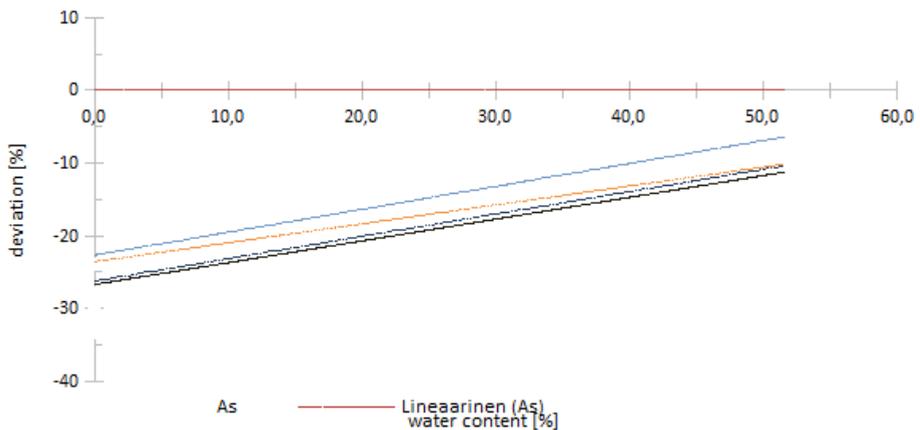


**Figure 6** Comparative hXRF measurements: field-, cup- and chemical-analytical values – Mo and As content in copper mine tailing material (dotted line: congruency of chemical-analytical value and hXRF value)

### Selected results of the water saturation test

There is a clear, reproducible dependence of the element contents calculated by the hXRF device on the water content for arsenic, copper, iron, lead, potassium, titanium and zinc (fig. 7; Ti and K not shown). All mentioned elements show a relatively constant decrease in the measured element content with increasing water contents compared to the dry sample. The maximum deviation in a rather saturated state of the sample is approximately 30 %. The nominal content of approx. 1600 ppm Pb, determined with hXRF cup measurement and chemical analysis, apparently decreases to a value of about 1100 ppm. However, this behavior can only be confirmed for fine material < 20  $\mu\text{m}$  fraction. In the case of coarser samples, the specific, linear behavior like for the < 20  $\mu\text{m}$  fraction was not observed. It is much more difficult to define a concrete function.

Aluminum, a comparatively light element, shows greater fluctuations but a similar trend with high water contents. Calcium, sulfur and silicon (not shown here) are problematic. In contrast to the other elements, samples with a water content between 0 % and 15 % were characterized by element contents higher than the content of the actual dry sample, whereas rather wet samples with a water content > 15 % showed again a decrease in values. This behavior was confirmed by the hXRF output spectra. In order to explain this behavior, other materials (sediments, tailing material) need to be tested using the same methodology.



**Figure 7** Deviation of As, Cu, Fe, Pb and Zn content from dry initial sample

### Conclusions

The application of an hXRF device in the environmental and mining sector to determine elemental distributions and estimate element contents is reasonable. However, measured values should not simply be taken over and evaluated. Especially field-measured values are to be evaluated with the necessary distance and further processed. Using the example of As, Cd and Cu, it was shown that field values can deviate strongly from laboratory measurements. For copper content determination of drilling core samples (fig. 4) it becomes clear

that a recalibration of the data is reasonable. Cup-measurements with hXRF are preferable; a recalibration leads to an even better match between the hXRF value and the analytically determined value for certain elements (e.g. As, Ca, Cd, Cu, Mo, Pb, Sn, Zn). For a field method, hXRF obtains sufficiently accurate values for the estimation of the resource potential.

In addition, the water content in the field affects the results: Element contents (As, Cu, Fe, Pb, K, Ti, Zn) can have deviations of up to 30 %. The example of lead shows that in the nearly saturated state of 40% the real element content is underestimated by 30 %. The change in the content of Cu, S and Si with changing water content shows an unclear behavior, which is not yet understandable. However, this behavior is less obvious in coarser samples. Therefore, further measurements on other sedimentary materials have to be carried out and data sets have to be evaluated further.

These findings are relevant for the further characterization of tailings material. XRF technology is also to be used on large-scale in prospecting, e.g. in the case of direct-push methods, and therefore, a correction of the values depending on the water content is required.

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#### **References**

- Grimmer M, Haque Z, Ussath M, Hoth N (2015) Field portable X-Ray fluorescence analyzer (pXRF) –correction method for measurements in a silicon based matrix. Proceedings Colloquium Analytical Atomic Spectroscopy – CANAS 2015, Leipzig
- Kalnicky DJ, Singhvi R (2001) Field portable XRF analysis of environmental samples. *Journal of Hazardous Materials* 83: 93-122
- Ussath M, Wendler C, et al. (2015) Mobility of strategic elements in Chilean tailings in the context of secondary mining processes. In: Agreeing on solutions for more sustainable mine water management – Proceedings of the 10th ICARD & IMWA Annual Conference. – electronic document (paper 301), Santiago, Chile (GECAMIN)