



## Handheld ED-XRF spectrometers in geochemical investigation: Comparative studies for glacial deposits from Spitsbergen

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**Abstract:** This study presents the determination of the content of selected metals (Ba, Ca, Fe, Nb, Rb, Sr, Y, Zn, and Zr) in postglacial deposits from two glacial valleys (Ebbadalen and Elsadalén) in the Petunia Bay (southern Spitsbergen). The aim of the research was to experimentally check the usefulness of the handheld energy dispersive X-ray fluorescence technique in the study of samples from the polar zone, before performing the future field tests. Deposit analyses were performed (in parallel) with two handheld X-ray fluorescence spectrometers from different manufacturers, to investigate the accuracy and reliability of the instruments. The statistical analysis of the results indicated that the measurements carried out with two spectrometers were statistically significantly different, which was probably due to the different calibration characteristics used by the manufacturers. However, the analysis of the spatial distribution of element concentrations using Geographic Information System tools showed that the distribution maps of elements concentrations were similar regardless of the spectrometer used in the analyses.

**Keywords:** Arctic, Svalbard, X-Ray fluorescence, metals, statistical analysis, spatial distribution.



## Introduction

X-ray fluorescence (XRF) spectroscopy has been broadly used in environmental studies to estimate the geochemical composition in a multitude of matrices and a wide range of elements (Marguí *et al.* 2016; Oyedotun 2018). There are many advantages of using the technique: (i) simultaneous multi-element determination for solid or liquid samples, (ii) sample preparation is simple, fast, and can be non-destructive, which preserves the samples for further analyses, and (iii) high accuracy, precision and low operating costs (Matsunami *et al.* 2010; Oyedotun 2018). Handheld energy dispersive X-ray fluorescence or hED-XRF (henceforth abbreviated as hXRF) spectrometer provides a precise, real-time, cost-effective chemical analysis (Hou *et al.* 2004; Vanhoof *et al.* 2013; Ravansari *et al.* 2020). Due to the above-mentioned features, the technique has been applied not only in the field, but also in the laboratory (Hou *et al.* 2004; Declercq *et al.* 2019; Ravansari *et al.* 2020), generating a large number of environmental data contributing to the increase of knowledge in basic and applied research.

The hXRF technique is used in environmental studies *sensu lato* such as environmental reconstruction, exploration of processes, evaluation of the environmental quality, and contaminants analysis (Weindorf *et al.* 2014). It constitutes a useful alternative to other spectrometric techniques (*e.g.*, atomic absorption or inductively coupled plasma) and allows the direct field studies without sample preparation, which significantly shortens the analysis time and lowers its cost (Weindorf *et al.* 2014; Ravansari *et al.* 2020). Despite hXRF limitations (*i.e.*, higher detection limits), correlations among hXRF results with those obtained via the other techniques have been already reported (Lemière 2018; Declercq *et al.* 2019), proving that the former method provides reliable outcomes, comparable to results from conventional laboratory analyses.

The measurements using XRF involve scanning the sample for few seconds, allowing the X-ray beam to ionize the sample atoms, causing the emission of a fluorescent X-ray with specific wavelength and energy for each element present in the sample (Hou *et al.* 2004). Over the last decades, advancement in the construction of XRF instruments enhanced their performance, versatility, and sensitivity. Moreover, although they operate based on similar principles, each manufacturer has its own technology, differing in software and hardware configurations, which can even lead to differences in the scope of the elements to be detected (Weindorf *et al.* 2014).

Previous studies, focused on the performance and accuracy of hXRF scanners, have provided valuable comparative data on the reliability of these instruments. Declercq *et al.* (2019) used three hXRF instruments from different suppliers to measure heavy and light elements in soils from disparate countries and environments. Overall, the instruments yielded acceptable results, independently of the soil characteristics. However, the varied performance of the

scanners resulted in dissimilarities in readings of the analytical concentrations, which the cited authors attributed to the technical aspects and configurations of each instrument. Another study (Sarala 2016) investigated the elemental composition of glacial deposits in northern Finland, next to the Arctic Circle, finding similar spatial distribution for most of the major and minor elements tested comparing two handheld XRF analysers.

Polar environments have unique characteristics (*e.g.*, limited direct anthropopressure and pollution), hence constitute the important objects of research aimed at determining the chemical composition of their various components, which contributes to understanding the functioning of the ecosystems (Clarke and Harris 2003; Walker 2005).

Applications of laboratory XRF in polar studies before 1990 were scarce, most of them being recent, basically not older than 30 years. Investigations of the Arctic and Antarctica using laboratory XRF analyses allow the determination of metals in abiotic sample matrices such as sediments (Cuven *et al.* 2010; Adamson *et al.* 2019), soils (Stark *et al.* 2008), ocean (Xie *et al.* 2006), snow (Drab *et al.* 2002), and also biological samples (*e.g.*, bird feathers) (Xie *et al.* 2008), and even much more. Nevertheless, studies on the geochemical composition of polar glacial deposits are still needed (Dowling *et al.* 2019), especially those using handheld XRF as the field technique.

Geochemical studies on glaciated areas offer opportunities for obtaining information on sediments changed through the retreat and melting of glaciers, that can even be used during the characterization of the composition of the earth's crust to determine provenance of rocks (Dowling *et al.* 2019). An important part of the scientific process is the reproducibility, and environmental studies are largely comparative, constantly contrasting results, experimental procedures, analytical methods etc. From this point of view, it is important to investigate the commensurability of the data provided by hXRF spectrometers produced by different manufacturers.

The aim of this study is to compare the results from parallel analyses of glacial deposits, collected in Elsa and Ebba glacial valleys in central Spitsbergen, to check the reliability of the data in the context of use of the handheld XRF in field geochemical studies. The investigations were performed using two XRF spectrometers from different manufacturers (Tracer III ED-XRF and Vanta XRF) simultaneously. The obtained results were subjected to the statistical assessment and analysis of the spatial distribution of determined elements.

## Materials and methods

**Samples.** — Samples of post-glacial deposits (n=94) were collected in Petuniabukta (Billefjorden) in the central part of Spitsbergen. The sampling points were located in the two areas: Elsadalén – Elsa glacial valley (42 samples

in the transect along Elsa river) and Ebbadalen – Ebba glacial valley (52 samples in the network in the southern part of the valley). Each sample was collected from the 30×30 cm square surface using plastic tools and containers, and labeled as A1000, A1001 etc., in line with the previous field studies rules. All samples were transported to the laboratory and stored in temperature of -20°C. Finally samples were analysed in parallel.

**Instrumental analysis.** — In this comparative study, two popular and used in numerous research projects handheld ED-XRF spectrometers were used. The first instrument was Tracer III ED-XRF spectrometer (Bruker AXS, USA). The calibration of Bruker Mudrock Trace was used with the following parameters: 15 s of signal acquisition, 12  $\mu$ A, 40 kV, filter 0.3048 mm Al and 0.0254 mm Ti. The measurement uncertainty was estimated to be below 10%. The second instrument was Vanta XRF analyser (Olympus, Japan). In this case, the GeoChem calibration with default conditions was used (8–40 kV, automatic filter selection). The estimated uncertainty was at the level of 5%.

**Methodology of measurements.** — This study aimed at comparing the results of detection of selected elements using two XRF spectrometers: (i) Bruker Tracer (abbreviated as t) and (ii) Olympus Vanta (abbreviated as v). The laboratory environment was controlled to ensure stability and comparability of conditions (temperature, humidity, spectrometer geometry etc.); all measurements were carried out at the same time in the laboratory. To minimize the effect of non-homogeneity of the sample on the measurement result, a similar geometry of radiation beam positioning was ensured in subsequent measurements using two spectrometers. Due to the different elemental range of Mudrock Trace (Bruker) and GeoChem (Olympus) calibrations, the following elements were selected for comparison: Ba, Ca, Fe, Nb, Rb, Sr, Y, Zn, and Zr, including both macro and trace components of deposits.

**Statistical analysis.** — Statistical tests were performed using Statistica 13.1 software (StatSoft, USA). First, the descriptive statistics were calculated, and this set comprised median, mean, and minimal and maximal values. Next, the Shapiro-Wilk test was performed to check data normality. To analyse the differences between the results obtained using two XRF spectrometers, the comparisons of two dependent samples via the sign test (ST) and Wilcoxon signed-rank (WSR) test were used (independently). To compare the concentrations of selected elements in deposit samples indicated by both spectrometers, the multidimensional analysis (principal components analysis, PCA) was run. The significance level  $\alpha=0.05$  was applied for all statistical tests.

**Spatial distribution analysis.** — Geographic Information System (GIS) tools were used to prepare maps of the spatial distribution of concentration of determined elements (minimum-maximum maps). The software Quantum GIS – QGIS 2.8 (Open Source Geospatial (OSGeo) was used to prepare the maps of elements concentration. The localisation of the sampling points was determined using GPS Etrex instrument (Garmin, USA).

## Results and discussion

In total, 94 unprocessed (raw) samples of the post-glacial deposits were analysed using two XRF spectrometers, and selected macrocompounds and microcompounds of deposits (Ba, Ca, Fe, Nb, Rb, Sr, Y, Zn, and Zr) were determined using built-in calibration curves. Altogether, 1692 values of concentration have been obtained and used in statistical analysis.

**Descriptive statistical analysis.** — The analysis of descriptive statistics helped to locate the essential differences between series of data generated by different spectrometers (Table 1). Overall, the results of elements determination obtained using Tracer spectrometer (t) was higher (from 20% to >200%) than those from the Vanta spectrometer (v). The median concentrations of Ba, Fe, Nb, Sr, Rb, and Zr were similar for both devices, however, the median values of Ca, Y and Zn differed. Taking into account the mean values of determined elements, the differences were indicated for Ba, Ca, Sr, Y, and Zn, whereas the similar level of the mean values were found for Fe, Nb, Rb, and Zr. The differences of mean values were most probably caused by the extreme (max) values of concentrations of determined elements. Unlike the median, this measure of central tendency is sensitive to outliers and extreme values.

Table 1

Descriptive statistics of the results of hXRF determinations provided using  
v – Vanta spectrometer and t –Tracer spectrometer.

| mg·kg <sup>-1</sup> | Min  |       | Median |       | Mean  |       | Max    |        |
|---------------------|------|-------|--------|-------|-------|-------|--------|--------|
|                     | v    | t     | v      | t     | v     | t     | v      | t      |
| Ba                  | <1   | <1    | 328    | 313   | 327   | 617   | 822    | 2722   |
| Ca                  | 3552 | 10582 | 57590  | 80314 | 52189 | 71230 | 167972 | 180399 |
| Fe                  | 8231 | 14159 | 20741  | 22320 | 20774 | 21970 | 90202  | 53036  |
| Nb                  | <1   | 5     | 10     | 8     | 10    | 8     | 37     | 11     |
| Rb                  | <1   | 28    | 48     | 50    | 48    | 51    | 116    | 87     |
| Sr                  | 31   | 69    | 121    | 138   | 109   | 127   | 205    | 258    |
| Y                   | <1   | 12    | 18     | 29    | 19    | 30    | 53     | 48     |
| Zn                  | <1   | 1     | <1     | 42    | 36    | 46    | 158    | 153    |
| Zr                  | 48   | 115   | 221    | 219   | 247   | 244   | 667    | 632    |

**Statistical analysis of the differences.** — The results from Shapiro-Wilk test revealed the non-normal distribution of data, so nonparametric tests were used. The sign test (ST) showed that concentration readings of Ba, Rb, Zn, and Zr were similar for both spectrometers ( $p=0.68$ ,  $0.46$ ,  $0.47$ , and  $0.41$  respectively). The Wilcoxon signed-rank (WSR) test results were different and showed the lack of

statistically significant differences in concentration readings of Rb and Zr only ( $p=0.17$  and  $0.23$  respectively). Overall, both tests showed, that most of the results obtained using two spectrometers were different, data for Rb and Zr being the only exceptions, as far as statistical significance was concerned. These differences are likely to be due to calibration characteristic (systematic errors), not exactly adapted for the specific matrix of post-glacial deposits. Therefore, the results of analyses using handheld XRF spectrometers should be considered as semi-quantitative.

**Exploratory statistics.** — In the exploratory statistical analysis, the high accuracy of the results is, under certain circumstances, not important. Exploratory analysis can be performed for a dataset with a systematic error, for it does not affect its result. Simply, the obtained data are not accurate due to interference or calibration characteristics, but the influence of these factors is (by definition) the same for the whole series of samples. To investigate the character of data of the concentrations of selected elements in post-glacial deposit samples, the principal components analysis (PCA) was applied. For data obtained by Vanta spectrometer (v), the samples A1023, A1029, A1030, A1032, A1033, A1034, A1035, and A1036 have been indicated as different based on concentrations of Ba, Ca, Fe, Nb, Rb, Sr, Y, Zn, and Zr. The same analysis performed for data obtained using Tracer spectrometer (t) indicated the samples A1015, A1030, A1032, A1033, A1034, A1035, and A1036 as different based on the concentration of determined elements (Fig. 1).

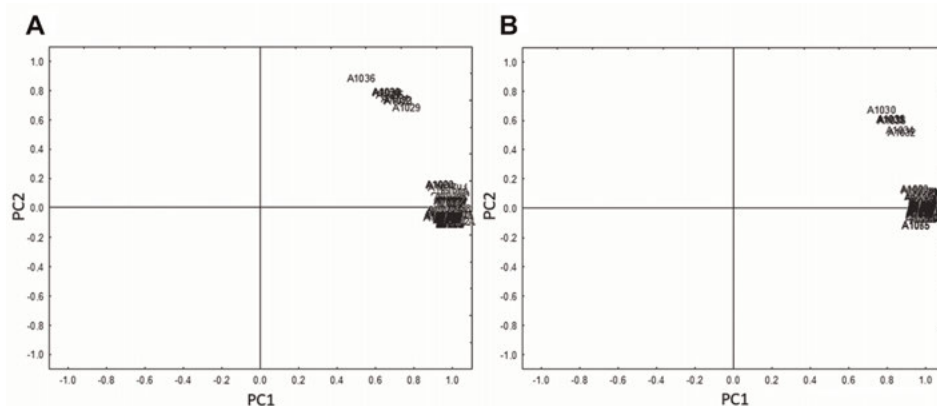


Fig. 1. Results from principal components analysis (PCA) for analyses using two spectrometers: **A** – for Olympus Vanta data, **B** – for Bruker Tracer data.

To summarize, for 94 analysed samples, the differences in results of the exploratory data analyses were limited to three samples only (A1015, A1023, and A1029). PCA outcomes (in both analyses the first two principal components explained over 90% of the variability) indicate that results obtained using different spectrometers were similar and almost the same group of samples was ‘highlighted’ in both of them. Although the values resulting from analyses

provided using two spectrometers were different, it is still possible to indicate the outlier samples, based on chemical composition recognised in XRF analysis (Michałowski *et al.* 2020).

**Analysis of the spatial distribution of elements.** — To compare the spatial distribution of concentration of elements determined by two spectrometers, the minimum-maximum maps have been prepared using the GIS tools (Fig. 2).

The maps of spatial distribution of selected elements were very similar and indicate the same areas with high and low concentration of elements determined, regardless of the spectrometer used in the analysis. Although the results of analyses carried out with the use of both devices differ from each other, they allow for a coherent and similar assessment of the distribution of elements on the tested surface. Similar conclusions have been already formulated for archaeological artefacts analysis (Kozak *et al.* 2016).

The problem of semi-quantitative analysis using XRF has long been recognized (Coetzee *et al.* 1986). The necessity of adjusting the calibration to the analysed matrix was pointed out, which allowed for obtaining acceptable compliance of the results from the analyses using various analytical techniques (Brown *et al.* 2010; Fayyaz *et al.* 2019; Cheng *et al.* 2020). Due to the heterogeneity of geological samples, to achieve consistency of results, it is necessary to increase the measurement precision by using more repetitions (Ramsey *et al.* 1995), or pre-milling of samples (Coetzee *et al.* 1986), which when using handheld XRF instruments significantly reduces their usefulness in fieldwork. The XRF technique may be useful in field analyses, however, the results obtained need to be confirmed in laboratory analyses using other measurement techniques (Mäkinen *et al.* 2006). In addition, the calibrations made by the manufacturers of various spectrometers require empirical readjustment, matching them to the tested matrix. Unfortunately, such recalibration is time-consuming and requires specialized knowledge and access to appropriate laboratory equipment (Declercq *et al.* 2019).

## Conclusions

The results presented in this study demonstrated that samples analysed using handheld XRF spectrometers from different manufacturers exhibit statistically significant differences in respect to concentrations of the majority of determined elements. This confirms the semi-quantitative nature of the outcome obtained in ED-XRF handheld analyses. Despite the differences in the element concentrations obtained using different spectrometers, the results reflect properly the spatial distribution of the elements in the studied area, making XRF a useful tool in geochemical studies.

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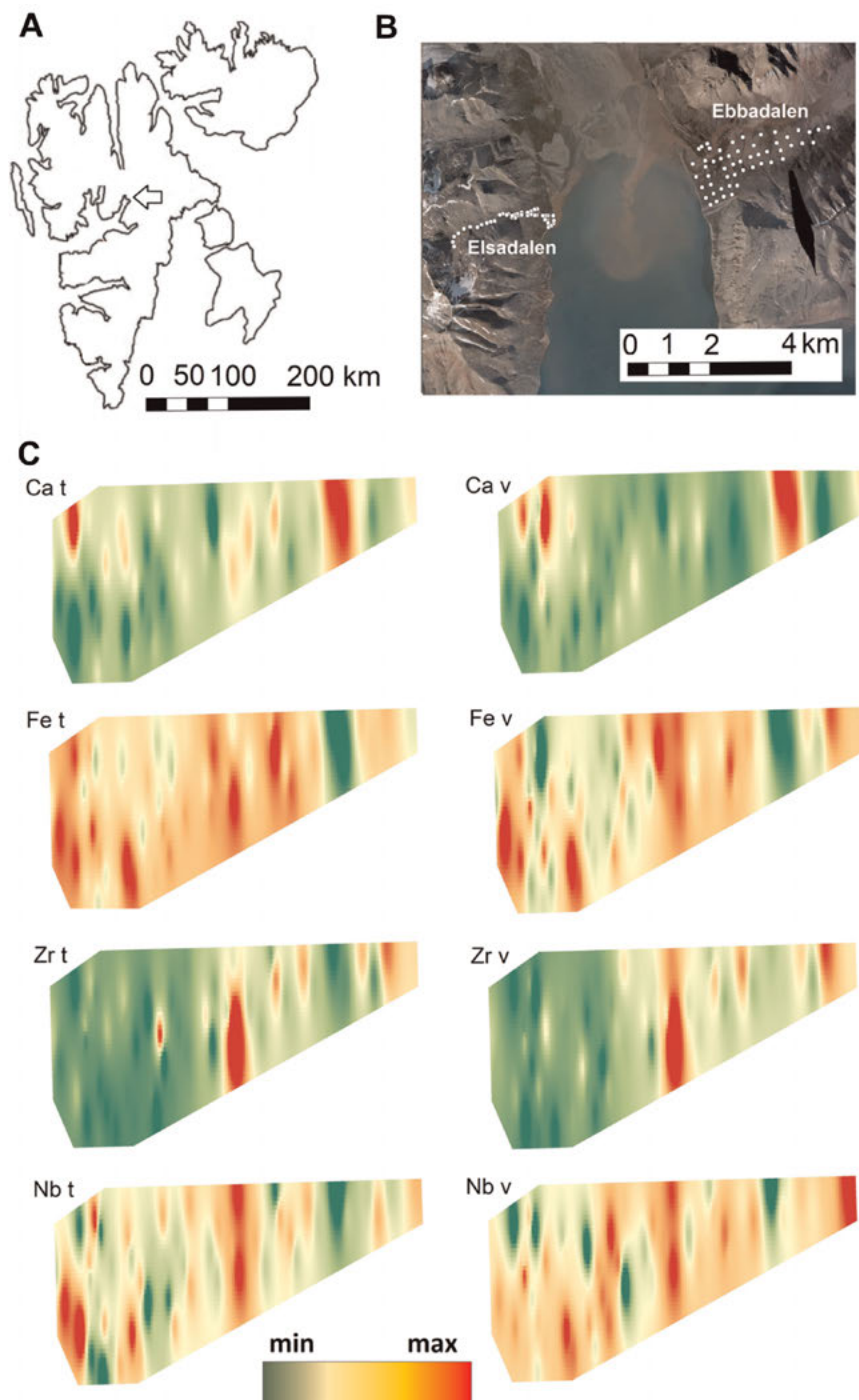


Fig. 2. Graphical presentation of the spatial distribution of elements (QGIS maps): **A** – location of Ebba valley, **B** – location of sampling points in Ebba valley, and **C** – maps of the spatial distribution of selected elements to Bruker Tracer (t) and Olympus Vanta (v).



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