

Handheld ED-XRF spectrometers in geochemical investigation – the comparative studies for glacial deposits (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, Zr in postglacial deposits from two glacial valleys (Ebbadalen and Elsadalen) in the Petunia Bay (southern Spitsbergen). Deposits analyses were performed using X-ray fluorescence (XRF) in parallel with two portable spectrometers from different manufacturers to investigate the accuracy and reliability of the instruments. Statistical analysis of the results indicated that the measurements carried out with two spectrometers are statistically significantly different, which is probably due to the different calibration characteristics used by the manufacturers of XRF spectrometers. However, the analysis of the spatial distribution of element concentrations using Geographic Information System (GIS) tools showed that the distribution maps of element concentrations were similar regardless of the spectrometer used in the analyses.

Keywords: X-Ray fluorescence, metals, Arctic, glacial deposits, statistical analysis

Introduction

X-ray fluorescence (XRF) spectroscopy is broadly used in environmental studies to estimate the geochemical composition in a multitude of matrices and a wide range of elements [1,2]. There are many advantages in using the technique: 1) simultaneous multi-element determination for solid or liquid samples 2) sample preparation is simple, fast, and can be non-destructive which preserves the samples for further analysis 3) high accuracy, precision and low operating costs [2,3]. Handheld ED-XRF spectrometer provides a precise, real-time, cost-effective chemical analysis [4–6]. Due to the countless benefits, the technique has been applied not only in the field but also in the laboratory [5–7], generating a large number of environmental data contributing to the increase of knowledge in basic and applied research.

Most of the application of XRF analysis in environmental science focused on the evaluation of the environmental quality and contaminants analysis [8]. XRF instruments are a useful alternative to other spectrometers (e.g. atomic absorption or inductively coupled plasma) considering that the latter techniques require sample preparation leading to higher analysis time and cost comparing with the former technique [8,9]. And besides XRF limitations (i.e. higher detection limits) correlations among XRF results with the cited techniques are already reported [7,10] proving that XRF provides reliable and comparable results to conventional laboratory analysis.

The measurements by XRF involve scanner 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 [5]. Advances in XRF instruments over the last decades enhance their performance, versatility and sensitivity. And, although they operate with similar principles, each manufacture has its own technology differing in software and hardware configurations which can even identify different sets of elements [8] which can even lead to different brands to identify different sets of elements.

55 Previous studies compared the performance and accuracy of XRF scanners providing
56 data on the reliability of these instruments. Declercq and others used three XRF instruments
57 from different suppliers to measure heavy and light elements in soils from different countries
58 and environments. In general, the instruments presented acceptable results independently of
59 the soil characteristics. However, the varied performance resulted in dissimilarities in the
60 analytical concentrations among the scanners which the authors attributed to the technical
61 aspects and configurations of each instrument [7]. Similarly, one study characterized the
62 elemental composition of glacial deposits in northern Finland next to the Arctic Circle finding
63 similar spatial distribution to most of the major and minor elements tested comparing two
64 handheld XRF analysers [11].

65 Polar environments have unique characteristics being the determination of the
66 chemical composition important to understand these ecosystems that recently have been
67 threatened [12].

68 Applications of XRF in polar studies before 1990 are scarce, most of the studies are recently
69 from the last 30 years basically. Investigation of the Arctic and Antarctica by XRF analysis
70 allows the determination of metals in abiotic samples matrices such as sediments [13], soils
71 [14], ocean [15] and snow [16], and also biological samples such as bird feathers [17]. But
72 studies on the geochemical composition of polar glacial deposits are still needed [18],
73 especially by XRF.

74 Geochemical studies on glaciated areas offer opportunities for obtaining information
75 on sediments changed through of retreat and melting of glaciers, and it can even be used to
76 represent the characterization of the composition of the earth's crust [18].

77 An important part of the scientific process is the reproducibility, and environmental
78 studies are constantly comparing results, experimental procedures, analytical methods and

others. In this context, it is important to investigate the commensurability of the data provided by XRF spectrometers produced from different manufacturers for reliable comparison.

Thus, this study compares the results of parallel analyses of glacial deposits collected in Elsa and Ebba glacial valleys in central Spitsbergen to check the data reliability of different equipment. The analyses were performed using two XRF spectrometers from different manufacturers (Tracer III ED-XRF and Vanta XRF) simultaneously. The obtained results were subjected to statistical analysis and analysis of the spatial distribution of determined elements.

Experimental

Instrumental analysis

In this comparative study two handheld ED-XRF spectrometers were used. The first instrument was Tracer III ED-XRF spectrometer (Bruker AXS, USA). The calibration Bruker Mudrock Trace was used with the following parameters: 15 s of signal acquisition, 12 μ A, 40 kV, filter 0,3048 mm Al and 0,0254 mm Ti. The measurements uncertainty was estimated below 10%. The second instrument was Vanta XRF analyser (Olympus, Japan). In the studies the GeoChem calibration with default conditions was used (8-40 kV, automatic filter selection). The estimated uncertainty was at the level of 5%.

Statistical analysis

Statistical tests were performed using Statistica 13.1 software (StatSoft, USA). Firstly, the descriptive statistic tests were performed and the following parameters have been defined: median, mean and minimal and maximal values. Secondly, data distribution character was examined. The Shapiro-Wilk test was performed to recognise data distribution.

To analyse the differences between the results obtained using two XRF spectrometers the comparison of two dependent samples - the sign test (ST) and Wilcoxon signed-rank (WSR) test was used regardless of each other. To compare the concentrations of selected elements in deposits samples indicated in the measurements using two spectrometers the multidimensional statistical analysis (principle components analysis PCA) was provided. The significance value $p=0.05$ 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). And 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 identified using GPS Etrex instrument (Garmin, USA).

Samples

Samples of post-glacial deposits ($n=94$) were collected in Petuniabukta (Billefjorden) in the central part of Spitsbergen. The sampling points are located in the two areas: Elsa glacial valley (42 samples in the transect along Elsa river) and Ebba glacial valley (52 samples in the network in the southern part of the valley). Each sample was collected from the 30x30 cm square surface using plastic tools and containers, and indicates with the description A1000, A1001... etc., according to the previous field studies rules. All samples were transported to the laboratory where they were analysed in parallel.

Methodology of measurements

This study aimed to compare the results of selected elements using two XRF spectrometers: 1) Bruker Tracer (t) and 2) Olympus Vanta (v). The laboratory environment was controlled to ensure stability and comparability of conditions (temperature, humidity,

spectrometer geometry etc.) and measurements were carried out at the same moment 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, Zr, including both macro and trace components of deposits.

Results and discussion

94 unprocessed 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, Zr) were determined using built-in calibration curves. In summary, 1692 values of concentration have been obtained and used in statistical analysis.

Descriptive statistical analysis

The descriptive statistical analysis - mean, median, minimum and maximum values showed the essential differences between two series of results generated by different spectrometers (Table 1). Generally, the results of elements determination obtained using Tracer spectrometer was higher (from 20% to >200%) than the results of the Vanta spectrometer. The median concentrations of Ba, Fe, Nb, Sr, Rb, and Zr were similar between both spectrometers, however the median values to Ca, Y and Zn were different between two spectrometers. Taking into account the mean values of determined elements the differences were indicated for Ba, Ca, Sr, Y and Zn the similar level of the mean values were found for Fe, Nb, Rb and Zr. The differences of mean values were probably caused by the extreme

(max) values of concentrations of determined elements. The use of descriptive analysis allowed to state that the sets of results obtained in measurements using two spectrometers differ from each other. However, the descriptive analysis did not allow assigning statistical significance to these differences. Hence the need to use further statistical analysis tools.

Table 1.

Analysis of the differences of results

The results of data distribution analysis (Shapiro-Wilk test) showed the non-normal data distribution so nonparametric tests were used. To recognise the potential differences between two series of measurements performed using two spectrometers the comparison of two dependent samples - the sign test (ST) and Wilcoxon signed-rank (WSR) test have been used. The ST test showed that the results of determination of Ba, Rb, Zn and Zr concentrations were similar between the spectrometers (ST test; $p=0.68$; 0.46 ; 0.47 and 0.41 respectively). The WSR test results were different than ST and showed the lack of differences of results of determination of Rb and Zr only ($p=0.17$ and 0.23 respectively). Generally, both tests showed, that most of the results obtained using two spectrometers, except Rb and Zr were statistically different. The statistical comparison of two dependent samples confirmed the conclusions of the descriptive analysis: in general, the results obtained using two XRF spectrometers are statistically different. The reason for these differences is 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 portable XRF spectrometers should be considered semi-quantitative.

Explorative statistic

In the explorative statistical analysis, the accuracy of the results is not important because the relations between concentration (not concentration values) of all the elements were

examined. If the results obtained in measurements by two spectrometers have a systematic error, the explorative statistical analysis may be provided successfully. To compare the character of data of the concentrations of selected elements in post-glacial deposits samples the multidimensional statistical analysis (principal components analysis PCA) was applied. For results obtained by Vanta spectrometer the samples A1023, A1029, A1030, A1032, A1033, A1034, A1035, A1036 have been indicated as different based on concentrations of Ba, Ca, Fe, Nb, Rb, Sr, Y, Zn, Zr. The same analysis provided for results obtained using Tracer spectrometer indicated the samples A1015, A1030, A1032, A1033, A1034, A1035, A1036 as the different based on concentration of determined elements. For 94 analysed samples the differences of results of explorative statistical analysis were determined for three samples (A1015, A 1023, A1029) only. PCA (in both analysis the first two principle components explain over 90% of the variability) results indicate that results obtained using different spectrometers were similar and indicates almost the same group of samples. Although, the values of results of analysis provided using two spectrometers were different, it is possible to indicate the outstanding samples, based on chemical composition recognised in XRF analysis [19].

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. The spatial distribution of concentration of elements is shown at Figure 1.

Figure 1.

The maps of spatial distribution of selected elements were very similar and indicates 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

two spectrometers differ from each other, they allow for a coherent and similar assessment of the distribution of elements on the tested surface. Similar conclusions were formulated for archaeological artefacts analysis [20].

The problem of semi-quantitative analysis using XRF has long been recognized [21]. The necessity of adjusting the calibration to the analysed matrix was pointed out, which allowed for obtaining acceptable compliance of the results obtained in the analyses using various analytical techniques [22–24]. Due to the non-homogeneity of geological samples, to achieve consistency of results it is necessary to increase the measurement precision by using more repetitions [25] or pre-milling of samples [21], which when using handheld XRF significantly reduces their usefulness in fieldwork. Additionally, the XRF technique may be useful in field analyses, however, the results obtained need to be confirmed in laboratory analyses using other measurement techniques [26]. In addition, the calibrations built by the manufacturers of various spectrometers require empirical recalibration, matching them to the tested matrix. Such recalibration is time-consuming and requires specialized knowledge and access to appropriate laboratory equipment [7].

Conclusions

The research presented in this paper showed that samples analysed using portable XRF spectrometers from different manufacturers differ statistically significantly in the results of the analysis performed. This confirms the semi-quantitative nature of the data 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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Table 1. The results of descriptive statistics with results of determinations provided using v - Vanta spectrometer and t –Tracer spectrometer

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

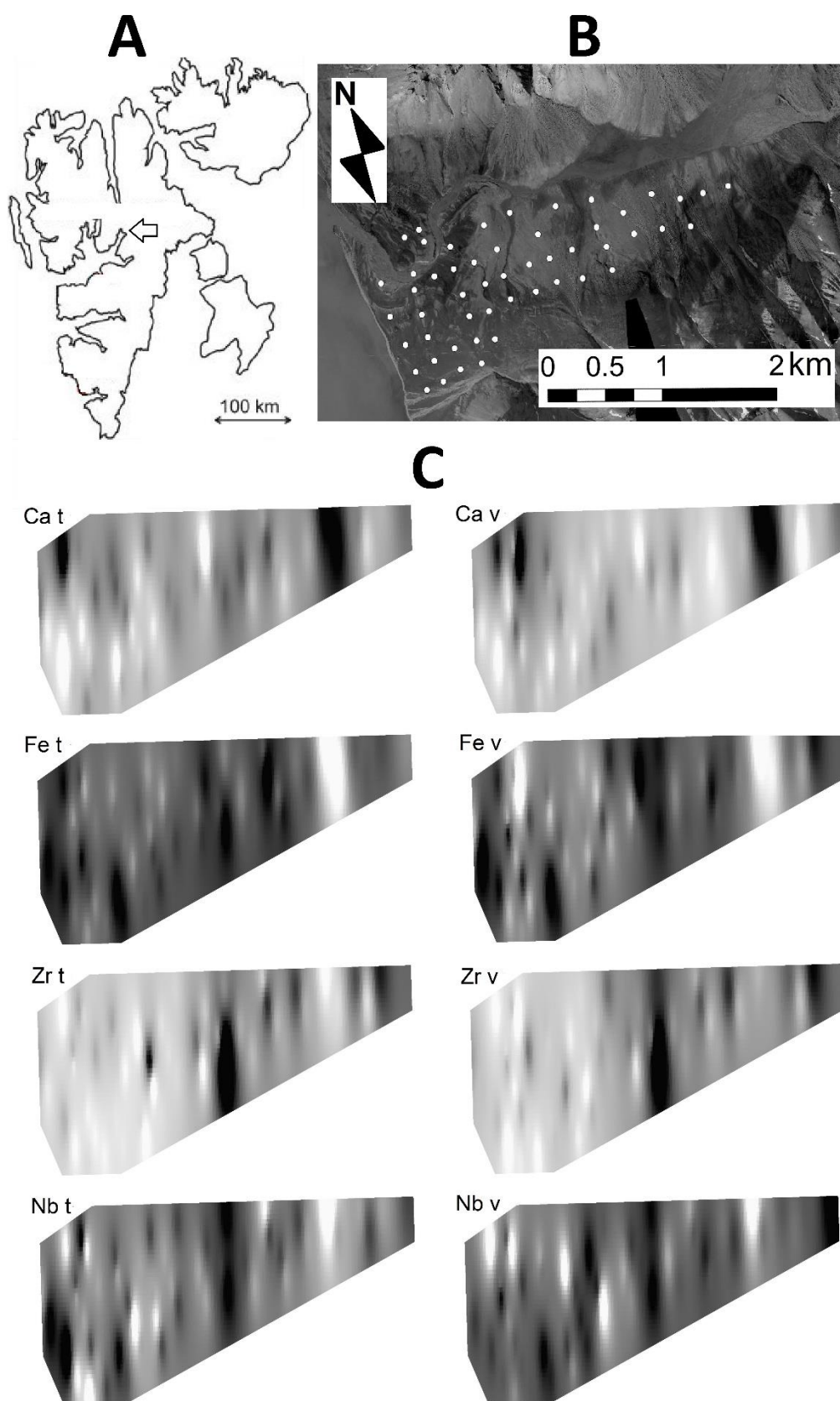


Figure 1. Graphical presentation of the spatial distribution of elements (QGIS maps)
 A - localisation of Ebba valley
 B - localisation of sampling points in Ebba valley
 C - maps of the spatial distribution of selected elements to Bruker Tracer (t) and Olympus Vanta (v)