

1 **Handheld ED-XRF spectrometers in geochemical investigation**
2 **– the comparative studies for glacial deposits (Spitsbergen)**

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15 **Abstract**

16 This study presents the determination of the content of selected metals: Ba, Ca, Fe, Nb, Rb,
17 Sr, Y, Zn, Zr in postglacial deposits from two glacial valleys (Ebbadalen and Elsadalen) in the
18 Petunia Bay (southern Spitsbergen). Deposits analyses were performed using X-ray
19 fluorescence (XRF) in parallel with two portable spectrometers from different manufacturers
20 to investigate the accuracy and reliability of the instruments. Statistical analysis of the results
21 indicated that the measurements carried out with two spectrometers are statistically
22 significantly different, which is probably due to the different calibration characteristics used
23 by the manufacturers of XRF spectrometers. However, the analysis of the spatial distribution
24 of element concentrations using Geographic Information System (GIS) tools showed that the
25 distribution maps of element concentrations were similar regardless of the spectrometer used
26 in the analyses.

27
28 **Keywords:** X-Ray fluorescence, metals, Arctic, glacial deposits, statistical analysis

30 **Introduction**

31 X-ray fluorescence (XRF) spectroscopy is broadly used in environmental studies to
32 estimate the geochemical composition in a multitude of matrices and a wide range of elements
33 [1,2]. There are many advantages in using the technique: 1) simultaneous multi-element
34 determination for solid or liquid samples 2) sample preparation is simple, fast, and can be
35 non-destructive which preserves the samples for further analysis 3) high accuracy, precision
36 and low operating costs [2,3]. Handheld ED-XRF spectrometer provides a precise, real-time,
37 cost-effective chemical analysis [4–6]. Due to the countless benefits, the technique has been
38 applied not only in the field but also in the laboratory [5–7], generating a large number of
39 environmental data contributing to the increase of knowledge in basic and applied research.

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

48 The measurements by XRF involve scanner the sample for few seconds allowing the
49 X-ray beam to ionize the sample atoms causing the emission of a fluorescent X-ray with
50 specific wavelength and energy for each element present in the sample [5]. Advances in XRF
51 instruments over the last decades enhance their performance, versatility and sensitivity. And,
52 although they operate with similar principles, each manufacture has its own technology
53 differing in software and hardware configurations which can even identify different sets of
54 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

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

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

87

88 **Experimental**

89 *Instrumental analysis*

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

97 *Statistical analysis*

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

102 To analyse the differences between the results obtained using two XRF spectrometers
103 the comparison of two dependent samples - the sign test (ST) and Wilcoxon signed-rank
104 (WSR) test was used regardless of each other. To compare the concentrations of selected
105 elements in deposits samples indicated in the measurements using two spectrometers the
106 multidimensional statistical analysis (principle components analysis PCA) was provided. The
107 significance value $p=0.05$ was applied for all statistical tests.

108 *Spatial distribution analysis*

109 Geographic Information System (GIS) tools were used to prepare maps of the spatial
110 distribution of concentration of determined elements (minimum-maximum maps). And the
111 software Quantum GIS - QGIS 2.8 (Open Source Geospatial (OSGeo) was used to prepare the
112 maps of elements concentration. The localisation of the sampling points was identified using
113 GPS Etrex instrument (Garmin, USA).

114 *Samples*

115 Samples of post-glacial deposits ($n=94$) were collected in Petuniabukta (Billefjorden)
116 in the central part of Spitsbergen. The sampling points are located in the two areas: Elsa
117 glacial valley (42 samples in the transect along Elsa river) and Ebba glacial valley (52
118 samples in the network in the southern part of the valley). Each sample was collected from the
119 30x30 cm square surface using plastic tools and containers, and indicates with the description
120 A1000, A1001... etc., according to the previous field studies rules. All samples were
121 transported to the laboratory where they were analysed in parallel.

122 *Methodology of measurements*

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

126 spectrometer geometry etc.) and measurements were carried out at the same moment in the
127 laboratory. To minimize the effect of non-homogeneity of the sample on the measurement
128 result, a similar geometry of radiation beam positioning was ensured in subsequent
129 measurements using two spectrometers. Due to the different elemental range of Mudrock
130 Trace (Bruker) and GeoChem (Olympus) calibrations, the following elements were selected
131 for comparison: Ba, Ca, Fe, Nb, Rb, Sr, Y, Zn, Zr, including both macro and trace
132 components of deposits.

133

134 **Results and discussion**

135 94 unprocessed samples of the post-glacial deposits were analysed using two XRF
136 spectrometers and selected macrocompounds and microcompounds of deposits (Ba, Ca, Fe,
137 Nb, Rb, Sr, Y, Zn, Zr) were determined using built-in calibration curves. In summary, 1692
138 values of concentration have been obtained and used in statistical analysis.

139

140 *Descriptive statistical analysis*

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

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

154 **Table 1.**

155 *Analysis of the differences of results*

156 The results of data distribution analysis (Shapiro-Wilk test) showed the non-normal
157 data distribution so nonparametric tests were used. To recognise the potential differences
158 between two series of measurements performed using two spectrometers the comparison of
159 two dependent samples - the sign test (ST) and Wilcoxon signed-rank (WSR) test have been
160 used. The ST test showed that the results of determination of Ba, Rb, Zn and Zr
161 concentrations were similar between the spectrometers (ST test; $p=0.68$; 0.46 ; 0.47 and 0.41
162 respectively). The WSR test results were different than ST and showed the lack of differences
163 of results of determination of Rb and Zr only ($p=0.17$ and 0.23 respectively). Generally, both
164 tests showed, that most of the results obtained using two spectrometers, except Rb and Zr
165 were statistically different. The statistical comparison of two dependent samples confirmed
166 the conclusions of the descriptive analysis: in general, the results obtained using two XRF
167 spectrometers are statistically different. The reason for these differences is likely to be due to
168 calibration characteristic (systematic errors) not exactly adapted for the specific matrix of
169 post-glacial deposits. Therefore, the results of analyses using portable XRF spectrometers
170 should be considered semi-quantitative.

171 *Explorative statistic*

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

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

190 *Analysis of the spatial distribution of elements*

191 To compare the spatial distribution of concentration of elements determined by two
192 spectrometers the minimum-maximum maps have been prepared using the GIS tools. The
193 spatial distribution of concentration of elements is shown at Figure 1.

194 **Figure 1.**

195 The maps of spatial distribution of selected elements were very similar and indicates
196 the same areas with high and low concentration of elements determined regardless of the
197 spectrometer used in the analysis. Although the results of analyses carried out with the use of

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

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

213

214 **Conclusions**

215 The research presented in this paper showed that samples analysed using portable XRF
216 spectrometers from different manufacturers differ statistically significantly in the results of
217 the analysis performed. This confirms the semi-quantitative nature of the data obtained in ED-
218 XRF handheld analyses. Despite the differences in the element concentrations obtained using
219 different spectrometers, the results reflect properly the spatial distribution of the elements in
220 the studied area, making XRF a useful tool in geochemical studies.

221

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231

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323

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

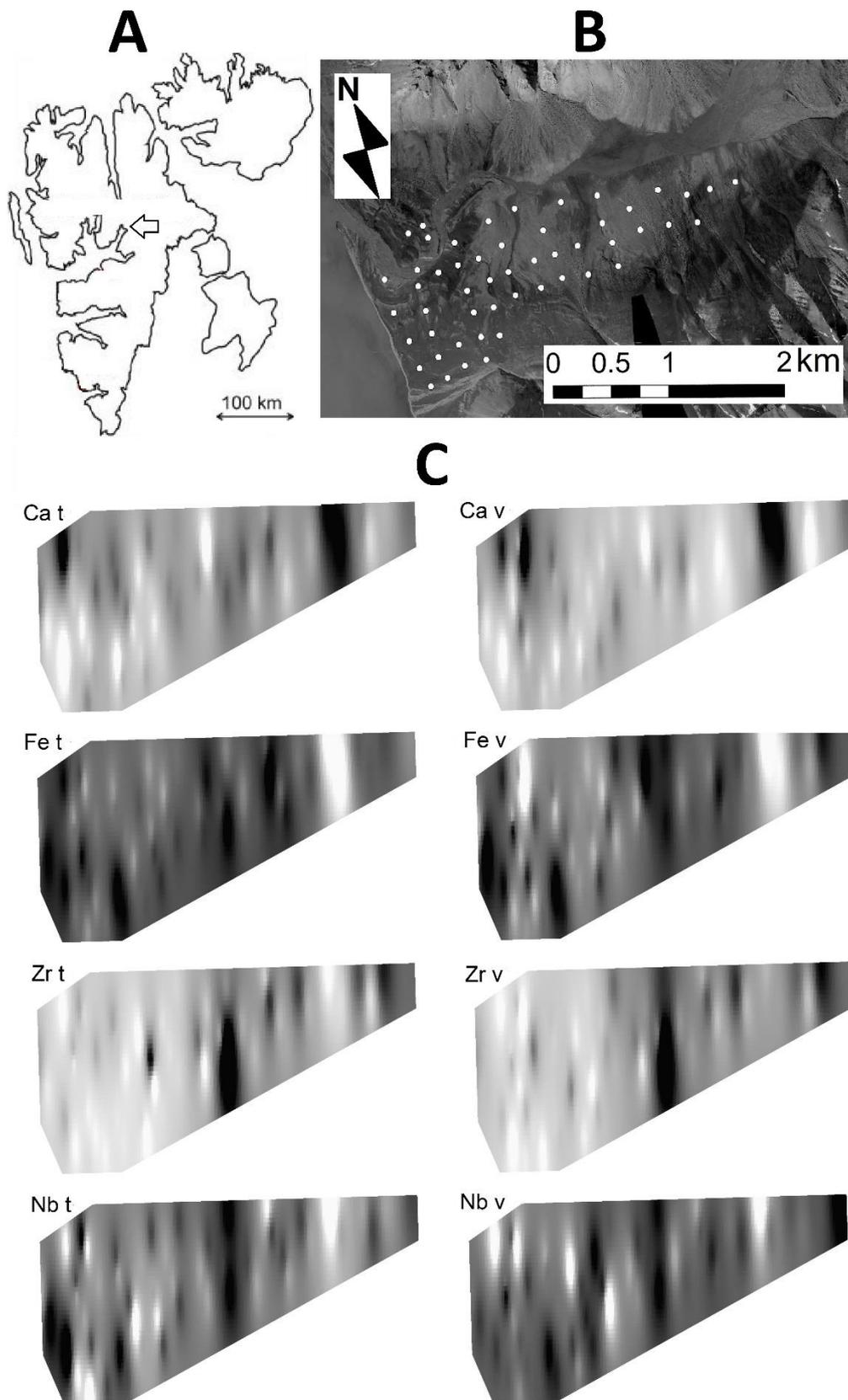


Figure 1. Graphical presentation of the spatial distribution of elements (QGIS maps)
 A - localisation of Ebba valley
 B - localisation of sampling points in Ebba valley
 C - maps of the spatial distribution of selected elements to Bruker Tracer (t) and Olympus Vanta (v)