

Joanna TRĄBSKA¹, Lucyna SAMEK², Beata OSTACHOWICZ²,
Erazm DUTKIEWICZ³

TXRF AND PIXE METHODS IN APPLICATION
FOR ARCHAEOLOGICAL HAEMATITE – GOETHITE ARTIFACTS

Abstract: 19 haematite-goethite archaeological artifacts were measured by non-invasive Particle Induced X-ray Emission (PIXE) and, requiring 20-50 mg of a sample, Total Reflection X-Ray Fluorescence (TXRF). Two samples were measured by both methods but the results are comparable only for trace elements. Chemical analysis was applied for further provenance studies.

Key words: Archaeometry, PIXE, TXRF, haematite.

INTRODUCTION

In the Dzierżysław-35 site, (Głubczyce Upland), flint, haematite-goethite (*ca.* 300 pieces) and other artifacts of Magdalenian Culture, Late Palaeolithic, were found (Ginter, Połtowicz 2002). Haematite-goethite artifacts are predominantly cherry or pink with red fresh fracture, soft, of platy texture. Previous examinations proved the presence of haematite, goethite, quartz, microcline, illite or kaolinite. Mictotexture is collomorphic, with tiny plates of clay minerals and very fine quartz grains. All samples seem to represent one genetic type, either of residual or precipitation or weathering type (Trąbska 2002). The two methods mentioned here have been known from only single archaeometric research but no comparison of them have been conducted so far.

MATERIALS AND METHODS

All samples were cleaned with distilled water and cotton wool. No sample preprocessing was necessary in the PIXE method. Artifacts were attached to an aluminium holder with cotton thread. Holder was covered by a 3M Scotch Tape to prevent samples from a contact with metallic parts. Artifacts were put together with the referential material inside the vacuum chamber of the apparatus. Measurements were performed in the external standard technique. Each sample was measured twice. The first measurement, without filters, aimed at determination of the

¹ *Archaeological Museum in Cracow, Senacka3 Str, 31-002 Cracow, email: trabska@ma.krakow.pl*

² *AGH University of Science and Technology, Faculty of Physics and Nuclear Techniques, Cracow.*

³ *Henryk Niewodniczański Institute of Nuclear Physics, Polish Academy of Sciences, Cracow.*

concentration of elements with $Z \leq 26$. In the second run, the elements of $Z \geq 26$ were determined. In this case, stacks of eight pieces of aluminium foil were used to reduce the X-ray signals from iron and from the light elements. As a referential material, the standard SD-N-1/2 from the International Atomic Energy Agency (IAEA) was used. It is a lake sediment, commonly used as standard in geological studies. The X-ray signal was induced by a 2.4 MeV proton beam accelerated in the 3.0 MeV Van de Graaff linear accelerator equipped with a radiofrequency source of ions. The beam spot was of about 3 mm diameter. Characteristic X-ray spectra were measured with a CANBERRA Si(Li) detector. The energy resolution was 165 eV FWHM for the 5.89 keV Mn $K\alpha$ line, in the regime of 800 counts per second. The characteristic X-ray spectra were collected using the Maestro II ORTEC Acquisition System and calculations were performed with the use of the program written by Kajfosz & Kwiatek (1987).

TXRF method required 20-50 mg of an artifact. Samples were wet digested in a Teflon bomb for 12 hrs, after being spiked by selenium as an internal standard. A mixture of $\text{HNO}_3 + \text{HF} + \text{H}_2\text{O}_2$ was used for sample digestion, then the solution was cooled and diluted by double-distilled and deionized water. From each sample solution 2 μl were pipetted onto three reflectors, dried and measured. A mean value of three determinations was taken as a result of the analysis. The TXRF spectrometer was calibrated with the use of lake sediment SL-1. A long fine focus Mo X-ray tube, operated at 55 kV and 40 mA was the excitation source, and Si/Li detector of 170 eV (FWHM) resolution was used. The counting time was 2000s. The QXAS software was employed for the data processing and quantification.

Table 1. Evaluation of homogeneity of analysed material (TXRF, concentration in $\mu\text{g/g}$, LLD means detection limit, in brackets – uncertainty of an analysis).

Element	3622a	3622b	3622c	Mean value	LLD
K	10400 (170)	13700 (800)	12200 (1100)	12100 \pm 1650	163
Ca	19300 (1000)	15100 (1100)	12400 (1600)	15600 \pm 3500	104
Ti	1500 (230)	2280 (340)	1700 (150)	1827 \pm 405	47
Cr	<LLD	<LLD	314 (73)	<LLD	31
Mn	610 (25)	800 (30)	2150 (120)	1187 \pm 840	29
Fe	4,9 (0,3) %	8,4 (0,1) %	13,7 (0,6) %	9 \pm 4,4 %	1 %
Ni	<LLD	<LLD	93 (13)	<LLD	18
Cu	84 (20)	120 (20)	95 (20)	100 \pm 18	11
Zn	56 (2)	107 (7)	80 (8)	81 \pm 25	9
Ga	8,8 (0,1)	15,1 (8,3)	12 (3)	12 \pm 3	6
Rb	66 (7)	95 (3)	74 (17)	78 \pm 15	8
Sr	320 (6)	260 (6)	217 (13)	266 \pm 52	8
Y	115 (4)	78,5 (3,5)	58 (4)	84 \pm 29	7
Pb	61,6 (4,3)	133 (36)	171 (13)	122 \pm 56	15

RESULTS

Though haematite-goethite artifacts macroscopically seemed to be homogenous, the three series of TXRF measurements of three different samples from powdered sample 3622 vary at the ppm level (Tab. 1). Concentration of elements in the two compared artifacts, 1760 and 2062, (Tabs. 2 & 3) may vary due to: a) expected samples unhomogeneity, b) different way of data acquisition (surface vs. volume), c) other factors that are being studied. The difference in Fe, K and Ca concentration are highest. SEM/EDS observation of cleaned surfaces (Trąbska 2002) prove that minor amount of clay minerals were still present but for such high discrepancy as in Fe content as 33.6% and 50.65% (sample 1760) another reason should be searched for.

Table 2. Results of analysis haematite samples by PIXE method (μ g/g).

Element	Sample									
	1760	2062	2507	2511	2587	2695	2724	2866	3138	3341
K	6200	19300	14200	19000	2700	19900	8000	14000	16100	18200
Ca	4700	2500	4600	900	2600	2500	1200	4200	4000	3300
Ti	2300	3300	2900	2700	1600	3200	1600	2200	2700	3300
Cr	<LLD	<LLD	<LLD	<LLD	<LLD	<LLD	<LLD	<LLD	<LLD	<LLD
Mn	12350	1500	700	200	13400	700	1250	450	3300	350
Fe	50.65 %	18.05 %	18.95 %	18.55 %	44.25 %	31.15 %	30.35 %	23.30 %	20.70 %	5.4% %
Ni	<LLD	<LLD	55	<LLD	204	72	<LLD	79	<LLD	59
Cu	48	65	33	<LLD	<LLD	<LLD	<LLD	<LLD	93	<LLD
Zn	125	174	55	<LLD	488	40	167	383	154	93
Ga	43	15	9	6	2	20	19	32	13	8
Rb	120	350	260	250	160	250	190	220	190	160
Sr	50	150	140	70	70	70	30	100	110	140
Pb	315	289	97	148	245	65	118	138		56

Table 3. Results of analysis haematite samples by TXRF method (μ g/g).

Element	Sample									
	x7	DZ35/ 97/5	1760	2062	3633	3384	5097	5173	5358	3384
K	19200 (400)	12500 (1000)	2070 (190)	9825 (151)	12100 (1650)	17150 (350)	23300 (1200)	20200 (1100)	20600 (800)	17150 (350)
Ca	15400 (600)	2520 (110)	<LLD	4143 (38)	15600 (3500)	5500 (760)	2880 (270)	3200 (500)	2800 (900)	5500 (760)
Ti	3100 (260)	2300 (180)	675 (12)	2163 (175)	1827 (405)	1755 (77)	2950 (290)	3260 (170)	3530 (425)	1755 (77)
Cr	230 (60)	<LLD	<LLD	268 (5)	<LLD	<LLD	<LLD	290 (13)	290 (10)	<LLD
Mn	700 (20)	1300 (70)	4140 (440)	803 (9)	1187 (840)	567 (26)	2580 (85)	290 (10)	420 (14)	567 (26)

Fe	8,5 (0,1) %	21,7 (0,9) %	33,6 (0,8) %	13.01 (0.13) %	9 (4,4) %	19,2 (0,2) %	12,9 (0,3) %	17,1 (0,2) %	15,2 (0,3) %	19,2 (0,2) %
Ni	72 (15)	<LLD	< LLD	< LLD	<LLD	<LLD	<LLD	<LLD	130 (1)	<LLD
Cu	51 (4)	<LLD	< LLD	56 (4)	100 (18)	<LLD	64 (23)	152 (22)	116 (13)	<LLD
Zn	81 (13)	115 (27)	< LLD	118 (13)	81 (25)	<LLD	142 (30)	53 (15)	83 (13)	<LLD
Ga	13,6 (1,5)	<LLD	< LLD	22 (1)	12 (3)	17 (1)	17 (1)	15 (2)	13 (1)	17 (1)
Rb	102 (7)	60 (8)	< LLD	119 (28)	78 (15)	90 (10)	106 (6)	101 (3)	120 (6)	90 (10)
Sr	285 (10)	84 (4)	76 (8)	137 (3)	266 (52)	122 (7)	100 (4)	98 (5)	120 (26)	122 (7)
As	90 (5)	25 (2)	< LLD		84 (29)	35 (10)	18,3 (3,5)	<LLD	<LLD	35 (10)
Pb	104 (2)	265 (8)	329 (17)	226 (9)	122 (56)	187 (9)	162 (7)	252 (48)	161 (1)	187 (9)

CONCLUSIONS

Compatibility of the TXRF and PIXE methods is valid for trace elements, though only an order of magnitude can be taken into considerable account. Concentration of main elements cannot be compared. Discrepancies result from unhomogeneity of samples, including natural admixtures of clay minerals, remnants of clays on their surfaces, present in low concentration even after cleaning, different sample areas that are measured or other, still unknown factors. A more efficient approach is being searched as an application of non-invasive or low-invasive methods is a basic requirement in archaeometric research. It seems, however, that for the provenance studies these results may be applied. The artefacts are supposed to come from a one type of an ore, connected with an area of weathering of mafic rocks.

REFERENCES

- GINTER B., POŁTOWICZ M., 2002: Sztuka ruchoma z magdaleńskiego stanowiska w Dzierżysławiu na Górnym Śląsku. W: Sztuka pradziejowa ziem polskich. Muzeum Początków państwa Polskiego. Gniezno 2002.
- KAJFOSZ J, KWIATEK W. M., 1987: Non-Polynomial Approximation of Background in X-Ray Spectra, Nucl. Instr. Meth. B22, 78.
- TRĄBSKA J., 2002: Sprawozdanie z badań czerwonych zabytków z Dzierżysławia. Raport KBN. Praca nie publikowana. Uniwersytet Jagielloński.