Characteristics and applications of FPXRF system

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Contents

- Characteristics of FPXRF system
- Analysis of geochemical samples in laboratory conditions
- Assessment of Cu pollution in over bank sediments by in situ measurements
- Identification of inorganic pigments in wall paintings by in-situ analysis
- Some data on aerosol analysis

Institute of Nuclear Physics (INP), Tirana

- Belongs to the network of scientific institutions of the Albanian Academy of Sciences
- Main duties:
 - Applied research in the field of atomic and nuclear physics, nuclear chemistry and electronics
 - Transfer of nuclear technology and knowledge
 - Education and Training

INP - Organization

- Departments:
 - Human and Environment Protection
 - Instrumental Analytical Methods
 - Technologies
 - Radiochemistry and Electronic
- <u>Divisions:</u>
 - Administrative
 - Library and Training

INP - Staff

- 27 researchers
 - 12 Experienced with degrees and titles
 - 15 Young
- 24 technical staff
- 19 administrative staff

Department of Instrumental Analytical Methods X-ray Fluorescence lab

- Equipments
 - Tube excited EDXRF system
 - TXRF system
 - Radioisotope excited EDXRF system
 - Field portable EDXRF system
- Staff
 - 2 researchers and 1 technician
- Applications
 - Geology and geochemistry (rocks, ores, crude oil, soils and sediments)
 - Environmental monitoring (aerosols, water)
 - Study of cultural heritage artifacts (pottery, coins, metals, pigments in icons and wall paintings, etc.)

X-ray detector and spectrum acquisition system

- Si-PIN X-ray detector (mod. XR-100CR)
- HV power supply and spectroscopy amplifier (mod. PX2CR)
- Pocket MCA 8000A
- Special software that works on a palmtop computer HP 200LX or on a laptop
- Company AMPTEC INC., USA.)



Si PIN detector characteristics



-100 V

- Area 7 mm^2
- Be window 1 mil
- Thermoelectrically cooled -30 °C
- High voltage
- Amplifier shaping time 20 μs

Thickness300 μmDetector extension 1.5 "

Detector performance



- FWHM 190 to 195 eV for Mn Kα at peak count rate 200 3000 cps
- Detector problems:
 - extended low energy tail at high count-rates peaks
 - high intensity peaks of Ni and Ag which are reduced by a collimator

Geometrical setup



- <u>Sources:</u>
- - Cd-109 (740 MBq)
- - Pu-238 or Am-241 (370 MBq)

excited elements K to Nb excited elements K to Br

- <u>The source-sample-detector geometrical setup 90</u>⁰
- - source-sample distance 20 mm
- - sample-detector distance
- - measuring window
- - angles of incidence and take-off 58,20 and 46,80
- 12 mm 20 mm

The spatial variation of the excitationdetection efficiency

- The results indicate that more than 90% of the information comes from an area with a diameter of about 12 mm and within this area the intensity changes more than 10 times from the maximum to the periphery.
- It also results that the edges of the window don't contribute to the measured intensity.



Spectrum fitting and quantification

- The spectra were fitted by the program AXIL
- The calculation of concentrations is performed by the program COREX which is based on the use of some fundamental parameters and some experimental calibrations obtained through the measurements of a set of thick standards prepared from pure elements or compounds.
 - Sensitivity = F(Z)
 - $\mu(Ec) = F(Ic)$
 - Z = F(Ir/Ic)

Sensitivities



Additional calibratios



Evaluation of the results

- A series of international geochemical standard reference materials were used for evaluating the analytical parameters and for testing the all analytical procedure.
- These include IAEA standards SI-1, Soil-5, Soil-7 and two sets of Chinese standard reference materials, GSS 1 ÷ 8 (soils) and GSD 1 ÷ 12 (sediments).
- The standard reference materials were measured for 2000 s using the Cd-109 radioactive source.

Detection limits



- The values of detection limits were evaluated from the values of background found under the peaks of different elements in the spectra of analyzed standards.
- The data show values from about 2500 ppm for K to about 4 ppm for elements from Rb to Zr; the calculated detection limits for Cu and Zn are respectively around 30 and 20 ppm.

Precision

| | GSS7 | | | | GSD3 | | | GSD6 | | |
|----|-------|--------|-------|-------|-------|-------|-------|-------|-------|--|
| | Rec | Mean | RSD % | Rec | Mean | RSD % | Rec | Mean | RSD % | |
| K | 0,158 | | | 1,938 | 1,51 | 7,0 | 1,92 | 1,89 | 4,0 | |
| Ca | 0,108 | | | 0,149 | | | 2,628 | 2,73 | 3,1 | |
| Ti | 1,92 | 2,25 | 1,5 | 0,604 | 0,58 | 1,4 | 0,441 | 0,45 | 2,9 | |
| Fe | 12,46 | 12,88 | 1,4 | 4,32 | 4,39 | 1,0 | 3,906 | 4,01 | 0,9 | |
| Cr | 389,5 | 411,0 | 15,1 | 82,6 | | | 180,5 | 143,0 | 17,6 | |
| Mn | 1691 | 1778,0 | 2,0 | 380 | 337,0 | 7,6 | 921,5 | 930,0 | 5,1 | |
| Ni | 262 | | | 24,3 | | | 74 | | | |
| Cu | 92 | 90,3 | 10,8 | 168 | 180,0 | 3,2 | 363,8 | 378,0 | 1,5 | |
| Zn | 135 | 144,5 | 10,6 | 49,4 | 63,4 | 15,8 | 136,8 | 145,7 | 12,1 | |
| Ga | 37,3 | 42,1 | 19,3 | 15,1 | 19,0 | 27,9 | 15,9 | 15,3 | 27,2 | |
| As | | | | 16,7 | 14,7 | 35,0 | 12,9 | | | |
| Rb | 15 | 15,3 | 13,5 | 75 | 77,7 | 1,5 | 102 | 111,3 | 1,0 | |
| Sr | 24,7 | 23,0 | 10,8 | 85,5 | 87,7 | 5,3 | 252,7 | 267,0 | 0,7 | |
| Y | 25,3 | 29,2 | 10,3 | 20,9 | 23,0 | 11,5 | 19,2 | 19,3 | 15,8 | |
| Zr | 302 | 300,5 | 2,7 | 209 | 208,3 | 2,7 | 161,5 | 156,3 | 3,3 | |
| Pb | 12,9 | | | 38 | 47,7 | 17,5 | 25,6 | 36,7 | 18,0 | |

Precision

- It can be seen that the precision for major elements is generally better than 5%.
- For most of the minor and trace analyzed elements the values of precision are within 10% and even at concentrations that approach the detection limits they are better than about 20%.
- Generally the mean calculated concentrations are in good agreement with the recommended ones.

Assessment of accuracy













Assessment of accuracy













Assessment of accuracy

- These data are considered to demonstrate excellent linearity (R2>0,99) with the exception of K and Mn.
- The lines have slopes close to 1 and very small intercepts, approaching to the ideal one to one line of equivalence i.e. the equivalence between analysed and expected values.
- These results show that a high degree of accuracy can be achieved during the analysis of geochemical samples by using the field portable instrument.

Quality control

- The quality control of our results was checked through the participation in the international proficiency testing program (GeoPT) organized by the International Association of Geoanalysts (IAG).
- Samples:
 - GAS Serpetinite
 - LOESS 1

Proficiency tests

| | Ge | eoPT12 roun | d | GeoPT13 round | | | |
|-------|-------------------|-----------------------|-----------|----------------------|-----------------------|-----------|--|
| | GA | AS Serpetinit | æ | LOESS – 1 | | | |
| | Reported values X | Assigned values Xa | Z - score | Reported values X | Assigned values Xa | Z - score | |
| K2O | | | | 1.2 | 1.3 | -2.8 | |
| CaO | 0.75 | 0.683 | 2.32 | 18.16 | 16.31 | 4.3 | |
| TiO2 | | | | 0.437 | 0.423 | 0.7 | |
| MnO | 0.091 | 0.085 | 1.22 | 0.063 | 0.0644 | -0.4 | |
| Fe2O3 | 7.77 | 8.021 | -1.07 | 2.1 | 2.1 | -0.1 | |
| Cr | 3150 | 2788 | 2.68 | | | | |
| Ni | 2300 | 2240 | 0.53 | | | | |
| Cu | | | | 21 | 11.3 | 7.7 | |
| Zn | 20 | 38.84 | -5.26 | 38 | 34.4 | 1.3 | |
| As | 125 | 121.1 | 0.42 | | | | |
| Rb | | | | 52 | 51.2 | 0.2 | |
| Sr | | | | 268 | 278.8 | -0.6 | |
| Y | | | | 22 | 23.18 | -0.5 | |
| Zr | | | | 300 | | | |

IN-SITU MEASUREMENT OF HEAVY METAL **CONTAMINATION IN OVERBANK SEDIMENTS OF THE MATI RIVER (NORTHERN** ALBANIA).

Objectives

- To evaluate the performance of our FPXRF system for in-situ determination of elemental composition of over bank sediments
- Comparison of in-situ results with those obtained in laboratory conditions
- Assessment of cooper pollution and localization of contamination 'hot-spots' in over bank sediments of Mati River.

THE SITE



- The main copper mining, processing and refining industries were situated in northern Albania along the river Fani, which is the main branch of the river Mati.
- The activities of the copper industry in that area began during 1920-1930 but from 1950 1960 the exploitation of the copper mines, the operation of the processing plants and copper metallurgy had a big increase until 1990 where all these activities have stopped.
- The wastes from all these activities flowed to the river and were accumulated in over bank sediments in the lower part of the Mati flow.

Sediment cross sections



- Three different cross-sections of the sediment layers, which should belong to different periods.
 - The first section
 - The two others

no contamination - older relatively high contamination up to our days

In-situ measurements

- Removal of the first 5 cm vertical layer
- Preparation of a fresh and smooth surface for XRF analysis
- Stable positioning of the measuring head on the layer's surface
- Two measurements, 800 to 1000 s, were performed at different positions of each layer, 5 to 10 cm from each other.
- The measurement protocol, both in the field and in the laboratory, includes:
 - 100 s measurement of a reference sample (Cu foil)
 - one reference material (GSS 7, GSD 3 and GSD 6) was run periodically before the measurements.
- Intensities are read from MCA and the spectra are saved.

Laboratory - sample collection and preparation

- The material from a surface with a diameter of 25 mm and 15 mm depth was collected at each measuring point.
- Compact pieces from some of the clay layers were also collected.
- The collected samples were put in plastic bags.
- In laboratory the samples were dried at 650C, disaggregated and the < 2 mm fraction was taken. This fraction was ground and homogenized in a pestle and mortar until all the material passed 150-mesh sieve.
- The determination of humidity and particle size distribution was performed for some of the samples.
- In laboratory the samples were measured for 2000 s as loose powders using a sample cup fitted with a 6µm thick Mylar foil.

Quality monitoring criteria

| | | Δ(log C) | | | | | |
|---------------------|--------------------------|-------------------------|--|--|--|--|--|
| Concentration range | Second grade standard | First grade standard | | | | | |
| < 3*DL | < ± 0.2 | < ± 0.3 | | | | | |
| > 3*DL | $< \pm 0.1$ | $< \pm 0.2$ | | | | | |
| 1 - 5 % | $< \pm 0.1$ | $< \pm 0.2$ | | | | | |
| > 5 % | < ± 0.05 | < ± 0.1 | | | | | |

Comparison of the in-situ with the laboratory

results

| | | Section 2 | | | | | | |
|----|---------|-------------|--------|---------|---------|-------|--------|---------|
| | Laye | r 2 - Mixed | clay | | Laye | | | |
| | In-situ | | Lab | | In-situ | | Lab | |
| | Average | RSD % | Powder | Δ(logC) | Average | RSD % | Powder | Δ(logC) |
| Ca | 1,81 | 16,8 | 1,82 | -0,004 | 1,64 | 3,0 | 1,27 | 0,110 |
| Ti | 0,28 | 21,8 | 0,35 | -0,096 | 0,48 | 12,0 | 0,41 | 0,067 |
| Fe | 10,75 | 1,8 | 10,25 | 0,021 | 11,09 | 9,7 | 10,69 | 0,016 |
| Cu | 847 | 58,0 | 903 | -0,028 | 231 | 5,6 | 260 | 0,088 |
| Zn | 329 | 83,9 | 321 | 0,012 | 168 | 16,6 | 158 | 0,027 |
| As | 166 | 4,5 | 173 | -0,019 | 137 | 0,5 | 181 | -0,123 |
| Se | 23 | 15,7 | 12 | 0,273 | 17 | 25,0 | 13 | 0,116 |
| Rb | 11 | 25,7 | 14 | -0,192 | 14 | 36,7 | 14 | -0,016 |
| Sr | 23 | 15,7 | 28 | -0,095 | 32 | 8,8 | 36 | -0,051 |
| Y | 10 | 28,3 | 9 | 0,046 | 12 | 18,4 | 13 | -0,053 |
| Zr | 31 | 50,2 | 49 | -0,199 | 53 | 14,8 | 78 | -0,172 |

The results of some major elements in the sediment layers

| | Ca % | | | Ti % | | Δ(logC) | Fe % | | |
|-------|---------|------|---------|---------|------|---------|---------|-------|---------|
| | In-Situ | Lab | Δ(logC) | In-Situ | Lab | | In-Situ | Lab | Δ(logC) |
| S1L1 | 3,69 | 2,48 | 0,173 | 0,53 | 0,49 | 0,039 | 8,38 | 6,77 | 0,093 |
| S1L2 | 4,50 | 3,22 | 0,145 | 0,48 | 0,49 | -0,007 | 8,21 | 6,49 | 0,102 |
| S1L3 | 3,40 | 2,69 | 0,102 | 0,47 | 0,44 | 0,028 | 7,75 | 6,75 | 0,060 |
| S2L1 | 1,07 | 1,32 | -0,091 | 0,35 | 0,49 | -0,145 | 8,90 | 10,31 | -0,064 |
| S2L2 | 1,81 | 1,82 | -0,002 | 0,29 | 0,35 | -0,084 | 10,75 | 10,25 | 0,021 |
| S2L3 | 1,64 | 1,27 | 0,111 | 0,47 | 0,41 | 0,063 | 11,09 | 10,69 | 0,016 |
| S2L4 | 2,24 | 2,05 | 0,038 | 0,45 | 0,36 | 0,095 | 9,97 | 9,36 | 0,027 |
| S2L5 | 2,83 | 2,60 | 0,037 | 0,53 | 0,43 | 0,097 | 8,05 | 7,85 | 0,011 |
| S3L1 | 1,50 | 1,08 | 0,143 | 0,49 | 0,46 | 0,029 | 14,06 | 11,72 | 0,079 |
| S3L2 | 1,47 | 1,68 | -0,058 | 0,24 | 0,34 | -0,163 | 10,77 | 10,53 | 0,010 |
| S3L3 | 2,56 | 2,05 | 0,096 | 0,47 | 0,43 | 0,043 | 12,02 | 11,32 | 0,026 |
| S3L4 | 1,70 | 1,30 | 0,117 | 0,38 | 0,41 | -0,040 | 13,74 | 12,73 | 0,033 |
| S3L5 | 1,74 | 1,45 | 0,079 | 0,32 | 0,43 | -0,130 | 6,24 | 7,47 | -0,078 |
| S3L6 | 1,97 | 1,69 | 0,067 | 0,48 | 0,56 | -0,070 | 7,96 | 7,13 | 0,048 |
| S3L7 | 1,55 | 1,46 | 0,026 | 0,52 | 0,49 | 0,030 | 6,32 | 6,11 | 0,015 |
| S3L8 | 3,33 | 2,57 | 0,113 | 0,68 | 0,58 | 0,073 | 8,10 | 7,32 | 0,044 |
| S3L9 | 2,30 | 2,33 | -0,006 | 0,47 | 0,54 | -0,061 | 7,84 | 7,60 | 0,014 |
| S3L10 | 2,36 | 2,42 | -0,011 | 0,63 | 0,51 | 0,093 | 8,40 | 7,28 | 0,062 |

The results of some trace elements in the sediment layers

| | Cu (ppm) | | | Zn (ppm) | | Δ(logC) | Zr (ppm) | | |
|-------------|----------|------|---------|----------|-----|---------|----------|-----|---------|
| | In-Situ | Lab | Δ(logC) | In-Situ | Lab | | In-Situ | Lab | Δ(logC) |
| S1L1 | 80 | 96 | -0,080 | 104 | 95 | 0,039 | 61 | 90 | -0,169 |
| S1L2 | 118 | 123 | -0,015 | 143 | 110 | 0,116 | 84 | 73 | 0,061 |
| S1L3 | 152 | 121 | 0,099 | 136 | 89 | 0,183 | 67 | 71 | -0,025 |
| S2L1 | 198 | 247 | -0,095 | 85 | 151 | -0,249 | 42 | 68 | -0,209 |
| S2L2 | 850 | 903 | -0,026 | 329 | 321 | 0,011 | 31 | 49 | -0,199 |
| S2L3 | 232 | 260 | -0,050 | 168 | 158 | 0,027 | 53 | 78 | -0,168 |
| S2L4 | 439 | 345 | 0,105 | 163 | 122 | 0,124 | 50 | 49 | 0,009 |
| S2L5 | 245 | 293 | -0,077 | 143 | 143 | 0,000 | 64 | 77 | -0,080 |
| S3L1 | 672 | 1042 | -0,190 | 287 | 293 | -0,008 | 61 | 64 | -0,021 |
| S3L2 | 1083 | 1130 | -0,018 | 652 | 520 | 0,098 | 36 | 48 | -0,125 |
| S3L3 | 625 | 653 | -0,019 | 413 | 492 | -0,076 | 50 | 53 | -0,025 |
| S3L4 | 519 | 519 | 0,000 | 287 | 324 | -0,053 | 50 | 58 | -0,064 |
| S3L5 | 3974 | 854 | 0,668 | 1402 | 268 | 0,718 | 35 | 76 | -0,337 |
| S3L6 | 123 | 151 | -0,090 | 149 | 156 | -0,019 | 91 | 92 | -0,005 |
| S3L7 | 156 | 139 | 0,050 | 132 | 112 | 0,071 | 106 | 100 | 0,025 |
| S3L8 | 164 | 136 | 0,082 | 115 | 123 | -0,030 | 100 | 91 | 0,041 |
| S3L9 | 171 | 174 | -0,009 | 178 | 123 | 0,160 | 86 | 87 | -0,005 |
| S3L10 | 163 | 190 | -0,066 | 161 | 137 | 0,069 | 81 | 84 | -0,016 |

Variation of some elements









Identification of "hot spots"



Factor Analysis from the in-situ data



- The first factor, with high loadings of Cu and Zn represents the discharges of cooper metallurgy
- The second factor, with high loadings of Fe, As and Se represents the discharges , mainly pyrites, of the ore processing plant.

Conclusions

- Large RSD values (20 50 %) are observed for most of the elements during the in-situ measurements in different points due to the sample heterogeneity.
- Despite this, an acceptable agreement is observed between average in-situ and laboratory values.
- It seems that the performing of two in-situ measurements improves the situation to an acceptable degree.
- The analysis of the differences between average in-situ and laboratory values shows that in some cases the differences are larger than the accepted limits.
- The increase of the number of in-situ measured points along the sediment layers can be a way for the improvement of the results.
- The in-situ XRF measurements provide a very good tool for cooper pollution assessment and for the identification of pollution 'hot-spots' in over bank sediments.
- Anyway the results should be treated with care because the heterogeneity of the layers or a bad sample collection can lead to doubtful results.

Application of FPXRF for pigment identification in wall paintings

"St. Theodore" church Berat



Historical data

- 'St. Theodore' church is situated within the surrounding walls of the castle, near the main gate.
- The single aisle church has been built during the first half of the 16th century on the foundations of an older one.
- The wall paintings on the northern and southern walls are attributed to an anonymous painter, while those on the eastern wall are painted by the famous painter Onufri during the first period of his activity.

Painted fragments on the eastern wall - Onufri

Pigment identification - Experiment

- Direct measurement on the wall-painting by FPXRF
- Collection of Q-tip samples on the measured points
- TXRF analysis of collected Q-tip samples
- Comparison of the results

The measurement and sampling points

Comparison of FPXRF and TXRF Green – 1

Green colour

- TXRF, FPXRF Ca, Fe (K, Mn, Cr, Sr)
- SEM-EDS Al, Si, Ca, Fe
- FTIR Green earth (Celadonite)

Comparison of FPXRF and TXRF Dark blue - 19

Blue colour

- TXRF, FPXRF Cu (Ca, Fe, Sr)
- FTIR Azurite

Comparison of FPXRF and TXRF White - 4

White colour

- FTIR Calcite
- TXRF, FPXRF Ca (Sr, Fe)

Comparison of FPXRF and TXRF Yellow - 6

Yellow colour

- TXRF, FPXRF Fe, Ca
- FTIR Bands 1100-900 and 3000 cm⁻¹
- Probably Yellow Ochre (FeOOH)

Comparison of FPXRF and TXRF Reddish – 14, Dark red - 23

Dark red, Reddish and Brown colours

- FTIR no information
- TXRF Fe
- FPXRF Fe with small amounts of Hg and Pb
- Reddish and brown probably a mixture of red ochre and red pigments with black carbon or painted in different layers
- Dark red probably red ochre mixed with black carbon

Comparison of FPXRF and TXRF Red – 5 Vermilion

Comparison of FPXRF and TXRF Plaster - 12

Plaster analysis

- SEM-EDS Ca (64-69%), Mg, Si
- FPXRF, TXRF Ca with small amounts of Fe and Sr
- FTIR Calcite, Silicates but also gypsum and oxalates
- Microscopy organic fibers (linen)

Results of plaster analyses

- Application technique fresco
- Deterioration of the wall paintings due to environmental conditions (air pollution (SO₂) and microorganisms)
- To much gypsum in sample No 18 suggests probably a mixture of calcite with gypsum in that part.

Summary

| Colour | No. sample | Identified key element | Other elements | Pigment |
|-----------|-------------------|------------------------|-------------------|----------------------|
| White | 4, 16 | Ca | Sr, Fe | Ca white |
| Black | 13, 18 | - | Ca, Sr, Fe | Probably C |
| Green | 1, 8, 15 | Ca, Fe | K, Mn, Ti, Cr | Green earth |
| Dark blue | 2, 19 | Cu | Ca, Sr, Fe | Azurite |
| Yellow | 6, 7, 20 | Fe | Ca, Sr, Mn | Yellow ochre |
| Red | 5, 10, 11, 17, 22 | Hg | Ca, Fe | Vermilion |
| Dark red | 23 | Fe | Ca, Sr | Red ochre + C |
| Reddish | 9, 14 | Fe | Ca, Sr, Pb, Hg | Red ochre + C |
| Brown | 3, 21, 24 | Fe | Ca, Sr, Mn | Yellow ochre +C |
| Plaster | 12 | Ca | Fe, Sr | Calcite |

Conclusion

- Inorganic pigments can be very well identified by FPXRF and TXRF
- Both techniques give the same results which are confirmed by other analytical methods
- FPXRF is very good for fast in-situ examinations
- Sometimes it can even detect under painted layers

Some data on aerosol analysis using FPXRF

Aerosol samples

Spectra of thin multielement standards FPXRF, Am-241 source

Evaluation of Detection limits FPXRF, Am-241 source

• Thin samples (Nuclepore filters)

- Ti Se
- -Rb-Sr
- Pb
- -Cd In

- $0.2 \sim 0.05 \ \mu g/cm^2$ $0.25 \sim 0.4 \ \mu g/cm^2$ $0.45 \ \mu g/cm^2$ $1.5 \ 2 \ \mu g/cm^2$
- $1.5 \sim 2 \,\mu g/cm^2$

Spectra of aerosol samples

Cellulose TFA 41

Nuclepore, $8\,\mu m$