Characteristics and applications of FPXRF system

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- 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
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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, $8\,\mu m$