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Detection of actinides and rare earths in natural matrices with the AGLAE new, high sensitivity detection set-up

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ABSTRACT

A series of granite samples (Grimsel and Äspö) enriched by sorption with ^{nat}U (10^{-3} M, 10^{-4} M, 10^{-5} M in solution) and La (10^{-3} M, 10^{-4} M in solution) has been scanned by PIXE over a surface of 1920×1920 mm^2 together with non-enriched Grimsel and Äspö granites and a glass standard. An assessment of minimum detection limits, MDL's, for several elements has been performed with the use of standard materials. Due to mapping and the high sensitivity of the new AGLAE detection system, U levels around 30 ppm can be detected from the whole PIXE spectrum (one low energy detector and four summed filtered detectors) while U reach grains, inhomogeneously distributed over the surface can be clearly identified through the multi elemental maps and analyzed separately. Even the nominally enriched samples have La levels below the MDL, probably because precipitation of the element (and not adsorption) mostly took place, and precipitates were eliminated after surface cleaning carried out before PIXE analyses.

1. Introduction

The new detection system attached to the AGLAE external micro-beam line at the C2RMF (France), is one of the fundamental parts of a multipurpose beamline with a high spatial resolution performance, beam stability and capability of multi-technique detection much higher than the previous facility. It opens interesting analytical options in the detection of trace elements which are relevant (rare earths) to the provenance attribution of various classes of cultural heritage objects (clays, glasses, ...) or to occasional but very specific and highly impacting dating problems (uranium/lead ratios) not excluding in any case, applications that fall outside archaeometry problems, namely environmental topics.

The main features of the new set-up [1] are:

(1) A multi detector system that implies a PIXE detection solid angle much wider than in any other similar set-up (a factor of 2–5); a higher events selectivity, given by the possibility of filtering individually up to 4 PIXE detectors; a double RBS detector, the new Ion Beam Induced Luminescence (IBIL) spectrometry and gamma spectrometry.
(2) Full mapping capability in air, assisted by a powerful event by event reconstruction software.

These features allow lower Minimum Detection Limits (MDL) which are highly beneficial to the analysis of cultural heritage objects, meaning generally a reduction of irradiation time. Paintings will then be studied without any damage to the pigments that have color change tendencies which is a major drawback of the previous system. Alternatively they could allow an increase in information collected at equal time, particularly considering the detector's fast response and therefore the potential for high beam currents when sample damage can be tolerated.

This kind of set-up should be advantageous for the detection of elements that are present in a geological, archaeological or artistic samples to the level of a few tens ppm. This is true in particular for the rare earths which are relevant to the provenance attribution of various classes of cultural heritage objects (clays, glasses, ...) and the actinides which are relevant in very specific and highly impacting dating problems and, more generally, critical environmental

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elements with special reference to the radionuclide mobility in deep geological formations hosting radioactive waste [2]. Geological materials are highly heterogeneous and consequently their retention of contaminants is heterogeneous as well. In this frame, the capabilities of the AGLAE set-up would allow an improved characterization of natural heterogeneous rock, detecting the presence of the elements of interest (actinides and rare earth) at concentration levels of tens of ppm. This provides a better definition of the initial system, avoiding biased interpretation of the retention properties of the material for the analysis of possible contamination. Additionally, if lower detection limits were achieved, new perspectives to evaluate retention of low solubility contaminants in a wider range of geochemical conditions would be opened.

A glass standard and a series of reference granite samples (Grimsel and Äspö), either enriched by sorption with ^{nat}U and La or kept natural, have been scanned by PIXE at the New-AGLAE detection system, to test measurement protocols and assess the MDL's allowed by the five detectors system.

Table 1
The concentration of some elements of interest in the standard glass NIST610, determined from Gupix in different detectors configurations.

	Th [ppm]	U [ppm]	Cu [ppm]	Zn [ppm]
CERTIFIED	457.2 ± 1.2	461.5 ± 1.1	444 ± 4	(433)
BE+H1-4	196 ± 10	201 ± 9	394 ± 9	429 ± 8
BE+H1	241 ± 18	239 ± 18	411 ± 13	421 ± 12
BE+H3	182 ± 19	207 ± 18	388 ± 13	423 ± 11
BE+H1-4	212 ± 3	209 ± 3	400 ± 5	438 ± 4
BE+H1	194 ± 6	195 ± 6	394 ± 7	433 ± 6
BE+H3	227 ± 6	200 ± 6	397 ± 6	435 ± 4
BE+H4	214 ± 6	214 ± 6	409 ± 7	445 ± 6
BE+H1-4	226 ± 3	218 ± 3	416 ± 5	460 ± 3
BE+H1	211 ± 6	208 ± 6	411 ± 6	454 ± 5
BE+H2	216 ± 6	207 ± 5	417 ± 6	456 ± 4
BE+H3	221 ± 6	219 ± 6	408 ± 6	459 ± 5
BE+H4	229 ± 6	214 ± 6	417 ± 7	467 ± 5
BE+H1-4	216 ± 4	218 ± 4	414 ± 5	461 ± 4
BE+H1	207 ± 7	206 ± 7	421 ± 7	456 ± 6
BE+H3	213 ± 6	207 ± 6	409 ± 6	455 ± 5
Average	213.5	210.8	407.1	446.2
St. dev	14.8	10.4	10	15

2. Materials and methods

2.1. Sample preparation

Beside the NIST 610 standard sample, a set of granites samples have been prepared.

Granite discs of around 11.8 mm in diameter and 1 mm thick were cut from a cylindrical sample extracted from a granite block (granodiorite type) coming from the FEBEX gallery located at the Grimsel Test Site Underground Research Laboratory (Switzerland) [3]. Other granite samples (diorite type) came from the Äspö (Sweden) underground research laboratory [4] and they were handled, transported and stored under anoxic conditions. The average natural occurrence of U is 8 ppm in Grimsel granite and 4.4 ppm in Äspo diorite, while natural La average composition is 175 ppm in Grimsel granite. No La data is available for Äspö. Uranium and lanthanum solutions were separately prepared dissolving either $UO_2(NO_3)_2{\cdot}6H_2O$ (MERCK) or $La(NO_3)_3{\cdot}6H_2O$ (MERCK) in HCl 0.1 M to a concentration of 0.1 M and, for sorption experiments, diluted in deionised water to concentrations 10^{-3} M, 10^{-4} M and 10^{-5} M, adjusting the final pH (between 5.18 and 6.50). Granite samples were first immersed in 30 mL of deionised water, extracted after one week and re-immersed during 25 days in 10 mL of La or U solutions at different concentrations (10^{-5} M, 10^{-4} M, 10^{-3} M). All experiments were carried out under atmospheric conditions. During this time U and La were incorporated to granite samples by sorption (and diffusion), but some precipitation cannot be ruled out. To eliminate precipitates over the surface, samples were cleaned with deionized water before PIXE measurements. Some reference samples were left without any tracer for characterization. Some of the samples were also carbon-coated for electron microscopy.

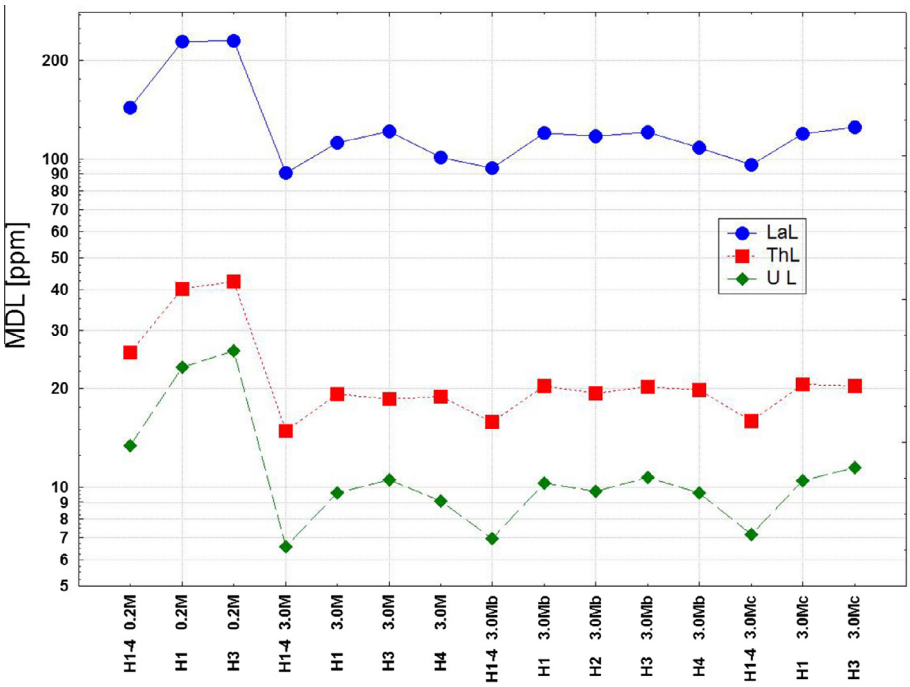

Fig. 1. The MDL's for LaL, ThL and UL lines as extracted from the NIST 610 PIXE spectra in different irradiation conditions and detectors configuration (see text for explanation).

Table 2
The composition of granites from Grimsel and Äspö, in various zones and in different enrichment conditions in terms of U or La.

Sample	Na	Mg	Al	Si	P	S	Cl	K	Ca	Ti	Mn	Fe	Co	Ni	Cu	Zn	Ga	As	Rb	Sr	Y	Zr	SnL	SbL	Ba	La	MDL La	Pb	Th	MDL Th	U	MDL U
	%	%	%	%	%	%	%	%	%	%	%	%	ppm	ppm	ppm	ppm	ppm	ppm	ppm	ppm	ppm	ppm	ppm	ppm	ppm	ppm	ppm	ppm	ppm	ppm	ppm	ppm	ppm
Grimsel zone 2	6.01	0.25	12.53	76.13	0.05	0.07	0.06	1.34	0.98	0.16	0.04	1.87			11	63	49	5	174	118	102		3851	346	226		29	33	21	27	42	20
Grimsel zone 4	2.61	0.12	16.48	69.62	0.05	0.11	0.10	8.81	0.36	0.08	0.04	1.01		2	14	37	49	16	748	56		13	4099	353	680		29	7		13		17
Grimsel zone 3	6.82		16.14	71.70	0.03	0.07	0.09	4.06	0.48	0.05	0.03	0.33		1	8	10	28	4	194	48			1283		303		16	10		3		4
Grimsel [ref.]	*4.1*	*0.5*	*14*	*71.8*	*0.1*			*4.2*	*1.6*	*0.3*	*0.07*	*2.2*							*700*	*85*	*126*	*250*			*650*	*175*			*24*		*8*	
Grimsel U 10-3 zone 1	6.65	0.06	18.07	67.41	0.06	0.12	0.03	5.04	0.90	0.30	0.03	0.74	78		2	18	38	6	394	72		24	4245	165	507		66	12		7	205	9
Grimsel La 10-3 zone 2	4.61	0.36	10.71	74.70	0.20	0.11	0.09	1.37	1.70	0.43	0.14	3.59	183		14	79	75	36	355	215	92	7	13496	2482	456	2364	59			70	75	48
Grimsel La 10-3 no C-coating	8.90		17.18	70.96		0.05	0.02	2.06	0.46		0.01	0.25			1	8	23		89	45			329	156	121	155	5	19		1		2
Grimsel La 10-4 no C-coating	6.29		14.23	75.11			0.01	3.51	0.42	0.01	0.01	0.29				4	22		159	43			474	86	183		10	11		2		3
Grimsel U 10-4 C-coated zone1	3.52	0.36	13.65	70.72	0.17	0.08	0.03	4.53	1.68	0.85	0.19	3.24				59	24	20	375	94	50	1689	6859				107		306	33	225	24
Grimsel U 10-4 C-coated zone 3	5.41		16.37	72.02		0.11	0.03	5.28	0.29	0.06	0.01	0.27	37		1	78	23		175	31			634		197		16	12		2	51	3
Grimsel U 10-4 C-coated zone 2	6.81	0.09	15.20	72.65	0.04	0.08	0.02	2.75	0.78	0.08	0.04	1.11	38			18	49		284	129	15	464	1264	344	483		31	39	26	13	505	12
Grimsel U 10-5 C-coated zone1	4.71		13.32	74.19		0.10	0.05	2.69	3.02	0.01	0.04	1.35	60		1	8	43	17	190	206			2448	1672	262		15			20	86	16
Grimsel U 10-5 C-coated zone 3	3.02		13.38	75.94		0.13	0.05	6.43	0.38	0.01	0.01	0.37	63		3	8	26	4	347	54			1028		582		18	20		3	307	6
Grimsel U 10-5 C-coated zone 2	4.42		10.29	80.55	0.05	0.14	0.06	2.53	0.47	0.30	0.03	0.67	149			15	27	5	260	56	12	330	3330		440		55	12	10	9	59	9
Aspo U 10-3 zone 2	4.13	3.87	20.05	44.33	2.43	0.21	0.06	1.72	5.02	0.95	0.11	13.32	172	65	8	334	123		568	4095		1652	7554	9845	1321		238	82	600	222	11336	146
Aspo U 10-3 zone 3	6.41	1.13	21.17	61.70	0.42	0.07	0.05	1.15	4.25	0.15	0.04	2.60		14	78	61	60		76	2087			772	155	986		50	32	123	24	4074	19
Aspo "fresh cut"	7.34	1.45	21.27	61.04	0.33	0.07	0.11	1.77	3.05	0.22	0.05	2.60		10	81	61	33		105	1163		36	3672	669	1072		44	15	20	11	9	8
Aspo [ref.]	*4.55*	*1.76*	*17.27*	*62.71*	*0.24*			*3.05*	*3.75*	*0.66*	*0.08*	*6.9*	*11*	*18*	*2*	*76*	*19*			*1052*	*22*	*168*			*1162*			*17*	*9.5*		*4.4*	

2.2. PIXE set-up

The standard glass and the granites were irradiated with 3 MeV protons over a surface of $1.920 \times 1.920\ mm^2$, with the configuration 1LE+4HE (the low energy detector and four filtered −50 mm Al- detectors, summed). Dose-equivalent of 10 Mc (counts of the Si Kα rays from the Si_3N_4 window) and current-equivalents from 4 to 7 kc/s were used. These corresponded to individual detector count rates of up to 40 kc/s.

The PIXE spectra were deconvoluted by the GUPIX program [5] assuming that all the elements were in oxide form and that the target was infinitely thick and the concentration sum was 100%. The four high energy spectra have always been added before deconvolution, but in several cases also individual high energy spectra have been analyzed. The oxide composition has been obtained by combining the results of low and high energy detectors with an already established procedure [6]. Taking advantage of the mapping capability (electrostatic + mechanical) and the high sensitivity of the detection system, we have selected map regions corresponding to specific minerals with MapPIXE acquisition and processing system [7] and the corresponding PIXE spectra have been analyzed using the same procedure.

3. Results and discussion

3.1. Standard glass

The NIST 610 standard, "Trace elements in Glass" is an alkaline glass including nominally 500 ppm of 61 elements of which 21 are certified. It produces as a consequence, rather complex PIXE spectra from which we have extracted, among other, the La, Th and U MDL's and concentrations in several combinations of the experimental set-up. We have operated once with a total dose of 0.2 Mc (coding 0.2 M) and three times with a dose of 3.0 Mc (coding 3.0 M, 3.0 Mb, 3.0 Mc) and analyzed the spectra corresponding to all the high energy detectors summed (H1-4) or only one of them (H_i, $i = 1,\ldots,4$). We observe in Fig. 1 both a factor ∼2 improvement when the dose is increased and again a factor of ∼1.3 improvement when the four detectors are summed. In the NIST 610 standard La detection limit is 90 ppm, 15 ppm for Th and 6 ppm for U at the best. As for the correspondence of measured and certified data, summarized in Table 1, Th average experimental concentration is 213 ± 15 ppm against a certified value of 457.2 ± 1.2 ppm and U average experimental concentration is 211 ± 10 ppm against a certified value of 461.5 ± 1.1 ppm. The concentration provided by our procedure on a homogeneous standard is reproducible under different analytical conditions, as shown in Table 1 (different combinations of the low energy detector BE and the high energy detectors H_i), so that the large discrepancy between certified and measured data for these particular elements (as opposed e.g. to Cu and Zn in Table 1) might be due to the poor accuracy of L lines production cross sections for both elements and not to the deconvolution procedure.

3.2. Granite samples

Several granite samples were scanned with the configuration 1LE+4HE and elemental concentrations and MDL's were extracted from the PIXE spectra produced by the whole scanned area. As seen in Table 2 the rock is non homogeneous and large variations of

Fig. 2. The Grimsel and Äspö granite samples with the zones marked for irradiation.

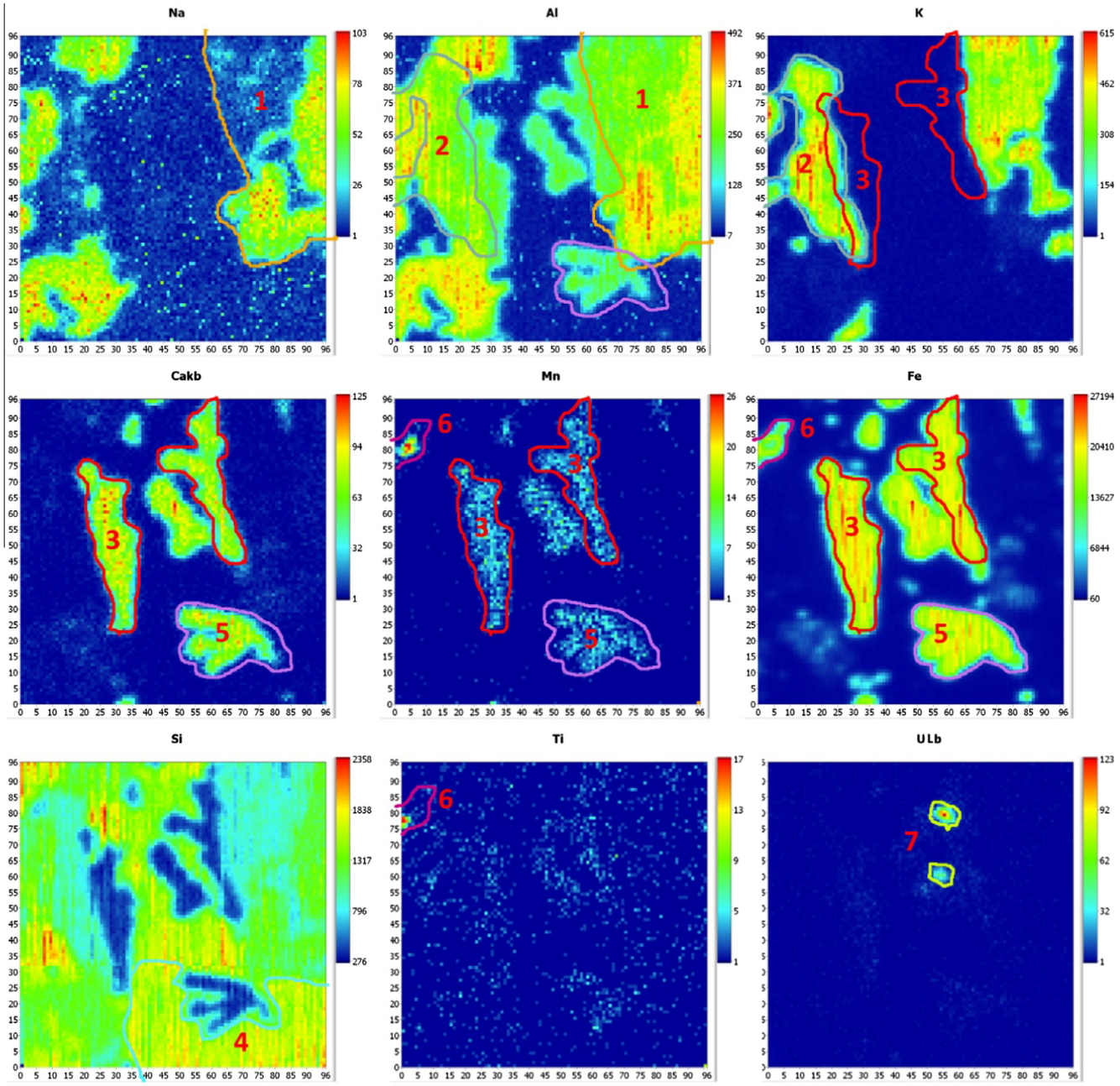

Fig. 3. Some elemental maps relative to the irradiation of Grimsel sample enriched with U at 10^{-5} M.

elemental oxides concentrations can be observed both for the natural rock constituents and for the enriched elements, if different zones of the same sample (Fig. 2) are scanned. Comparing our results for the natural rocks with those in literature we observed that the variations within the Grimsel PIXE results is of the same order of the difference between our results and those in literature [3]. We can only conclude that the PIXE results, although they are limited to small sample volumes, are within the same range with those provided by other techniques. As regards rare earths and actinides, La was detected only in the samples enriched in a 10^{-3} M solution but not in the 10^{-4} M case nor in the natural samples. This can be due to limited La sorption on granite as a result of precipitation on the surface. As mentioned in the experimental section, surface precipitates were eliminated prior to PIXE measurements. Th was detected in some samples, down to a lower limit of 10 ppm (Grimsel U 10^{-5} C-coated zone 2). U could be detected in many of the samples, down to a lower limit of 9 ppm (Äspö) "fresh cut").

Making use of the mapping facility [7], we have proceeded to the selection of specific areas of the samples, identified as granites constituent minerals and in particular those rich in U, as in Fig. 3, showing the maps relative to a sample Grimsel enriched with U at 10^{-5} M. The marked zones were identified from the elemental associations in the minerals as follows:

Zone 1: Plagioclase [$NaAlSi_3O_8$-$CaAlSi_2O_8$]
Zone 2: Feldspar [$KAlSi_3O_8$]
Zone 3: Epidote [$Ca_2Fe^{3+}Al_2Si_3O_{12}(OH)$]
Zone 4: Quartz [SiO_2]
Zone 5: Epidote family
Zone 6: Ilmenite [$FeTiO_3$]
Zone 7: Uranium

The selection allows the further reduction of the MDL's. The PIXE spectra generated from each zone are analyzed with the procedure described above for standards and whole spectra. In general we observe without problems the U, even at the lower enrichment value (10^{-5} M) and in the untreated natural samples (average 4 ppm), while La is only observed at the highest enrichment (10^{-3} M). In the first instance we have assumed that the much higher concentration values that we observe for the characteristic elements of each zone can be scaled down with the ratio between the zone area and the whole sample area and considered averages for the whole sample. So do the MDL's. The "effective" MDL are reduced, on the average, 12 times for La, 52 for Th and 33 for U, within all the zones considered.

4. Conclusion

The performances of the detection system associated to the AGLAE external micro-beam line have been tested making use of standards and of quite heterogeneous materials like granites kept in their natural forms or enriched with La and U at different concentrations. The PIXE detection capability for such trace elements is good and can be firstly improved by adding together the PIXE spectra. Higher improvements in the MDL's are obtained when, thanks to the mapping capability of the system, localized occurrences of an element may be identified and analyzed separately. Of some relevance is the interference of pile-up effects with the L lines of the investigated elements. In these cases further improvement could come from the reduction of counting frequency or pulse integration times. The study of MDL's with energy is a possible extension of this work.

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