INAA and ICP-MS Methods for Biological Tissues Studies

Maria I.G. Severo[1], Frédérique Barbier[2], Arno H. de Oliveira[3], Marie F. G. Loustalot[2],
Clemente G. Carneiro[3], Mario R. S. Silva[3]

[1] *Department of Biology Science - UESC Rodovia Itabuna Ilhéus Km 16, Ilhéus, Brazil, e-mail: severo@uesc.br*

[2] *Service Central d'Analyses, CNRS, B.P. 22-69390, Vernaison, France*

[3] *Department of Nuclear Engineering – UFMG, Av. Antônio Carlos 6627, Belo Horizonte, Brazil*

The advantages and drawbacks of using instrumental neutron activation analysis (INAA) and inductively coupled plasma mass spectrometry (ICP-MS) for accumulation in biological materials pollution studies are discussed. A Brazilian river, the Cachoeira, was chosen as the test-site, where the water is polluted by heavy metals originated by agricultural pollution. Four organs: muscle, gills, digestive glands and carapace of different crustaceans (*Macrobrachium carcinus* and *Ucides cordatus*) were studied. The experimental procedures used for each method and for each type of sample matrix are described. They were tested on several certified reference materials. The results obtained on these materials showed good agreement for many elements for which the two techniques are suited, and they were complementary for the other elements which are also of environmental interest. An element-by-element assessment is presented to indicate the precautions to be taken and the most convenient technique for each of them.

As vantagens e os problemas das técnicas de análise: ativação neutrônica (INAA) e espectrometria de massa associada a uma fonte de plasma induzido (ICP-MS), no estudo da acumulação de metais em materiais biólógicos são discutidas. O rio Cachoeira localizado no estado da Bahia foi escolhido por ter suas águas poluídas por metais pesados oriundos dos defensivos agrícolas utilizados na lavoura cacaueira e atividades artesanais clandestinas. Músculos, brânquias, glândulas digestivas e carapaças dos crustáceos *Macrobrachium carcinus* and *Ucides cordatus* foram analisados. Os procedimentos experimentais de análise para cada método e a preparação da amostra foram descritos. Estes procedimentos foram testados utilizando materiais certificados de referência. Os resultados obtidos mostraram que os métodos de análises (INAA e ICP-MS) são adequados e complementares no estudo da poluição devido a alguns elementos de interesse ambiental. A técnica mais adequada e as precauções a serem tomadas para a análise dos diversos elementos foram também mostradas.

1 Introduction

Environment studies have become increasingly important, in both industrialized and developing countries. These studies need to be able to analyze many elements over a very wide range of concentrations. Many methods can be used, but two appear to be particularly interesting for mineral pollutants: neutron activation analysis (NAA) and inductively coupled plasma mass spectrometry (ICP-MS). These methods can determine multiple elements and isotopes and are very sensitive. NAA has long been the only one sensitive and accurate enough for trace and ultra-trace analysis.

More modern and easier to use methods have never completely replaced NAA. ICP-MS, which combines excitation at the very high temperature obtained in a plasma of argon along with detection by mass spectrometry, has recently been adopted by a large number of laboratories. This method seems to have several advantages over NAA (great sensitivity for determining a wide range of elements, easy access and high sample throughout). The analytical procedures are well developed and were regularly tested on certified reference materials.

Both methods have been used to analyze samples of soils, sediments, plants and water. They were compared to identify the best method for analyzing a particular matrix and set of elements. For example, they were used to analyze the impact of rare earth elements on rice crops [1]. The use of small quantities of rare earth compounds as fertilizers (100-300 g/ha) increases the yield (plus 10-15%), quality of seeds and the resistance of rice to saline conditions. River pollution has been studied by analyzing sediments and water. The origin and extent of pollution were specified and quantified. Studies were carried out in Meknes city (Morocco), where the water is polluted by waste originated by rejects [2], from local craftsmen in Brazil on mining effluents in the State of Minas Gerais [3], and agricultural pollution caused by cacao growing in the State of Bahia [4]. Analysis of mosses provided a precise chart of the heavy metal deposits in France [5], complementing the data available for the whole of Europe. Lichens are also used as bio-indicators in volcanic areas [6].

Table 1. Neutron irradiation facilities - Pierre Sue Laboratory (n cm^{-2}.s^{-1})

	ENERGY	OSIRIS (70 MW)		ORPHEE (14 MW)		
Nuclear Reactor Channel		H$_1$	H$_2$	P1 and P2	P3	P4
Thermal neutrons	0.025 eV	$0.77.10^{14}$	$1.2 .10^{14}$	$1.23\ 10^{13}$	$I65.10^{,3}$	$2.5\text{-}10^{13}$
Epithermal neutrons	>0.1 eV	$.9\text{-}10^{12}$	$I4\ 10^{12}$	$6.15\ 10^{9}$	$8.25.10^{9}$	4510^{10}
Fast neutrons	>0.5 MeV	$9.6\ 10^{12}$	$2.3.10^{13}$	$3.5.10^{9}$	$8.2.10^{9}$	$1.2.10^{,\circ}$

The objective of this paper is to determine the concentration of Cu, Cr, As, Cd, Pb and other elements in muscle, gills, digestive glands and carapace of different crustaceans (Macrobrachium carcinus and Ucides cordatus) originated by agricultural pollution.

2 Experimental

Crustacean samples were collected from Cachoeira river watershed located at Bahia State in Brazil.

The environmental study was divided into five steps; analytical planning, representative sampling, sample preparation, analysis and data evaluation. Each step involved errors. The difficulty and susceptibility to error of each investigation depended on the sample matrix and content of elements to be analyzed. The difficulty of sample preparation depended on the form required by the analytical method used (solid for INAA and solution for ICP-MS). Heterogeneous solid samples, like soils, plants, biological materials or sediments, can be stored without any particular difficulty. The analytical step most susceptible to error was sampling. Some practical basic rules can be helpful: avoid contamination by the container, take a primary sample as large as possible, use a random division of the area to be sampled. International norms are available from AFNOR (*Association Française de Normalisation Paris*). The quality assurance of plant sampling and storage has been fully described by [7,8]. Sample washing, drying, homogenization aliquoting, and decomposition, were also potential sources of error. Certified reference materials (CRM) were used to check for sample loss or contamination.

3 Neutron activation analysis (NAA)

The muscle, gills, digestive glands and carapace samples were dried, crushed in an agate mortar and homogenized. Aliquots of powder (10-50 mg) were compressed to give pellets 10 mm in diameter. They were wrapped in high purity aluminum foil and placed in the shuttle used for irradiation, with the flux monitors and CRM prepared in the same manner.

All irradiations were performed in the ORPHEE and OSIRIS reactors at the Nuclear Center, Saclay. The Pierre Sue Laboratory is directly connected by pneumatic or hydraulic conveyors to six irradiation positions in these reactors. The characteristics of the neutron fluxes available are shown in Table 1. As environment research requires analysis of many samples, we used INAA. The irradiation and measuring conditions were chosen as a function of the samples analyzed and the elements determined.

Brief irradiations (30 seconds to 1 minute) (Al, Mg, Ti) determinations) in the in positions PI and P2 in the ORPHEE reactor were used for solid samples. Longer irradiations (3 to 72 hours) in positions P3 or P4 were used for Ce, Co, Cr, Fe, etc. Positions HI and H2 in the OSIRIS reactor was used for epithermal reactions ^{47}Ti(n,p)^{47}Sc, ^{58}Ni(n,p)^{58}Co, ^{54}Fe(n,p)^{54}Mn, etc. Irradiations were then often performed under a cadmium coating to select epithermal and rapid neutrons.

The gamma-radioactivity was measured with a 100 cm^3 coaxial ultra-pure germanium crystal coupled to a 4096 pulse-height analyzer. Several measurements were made on each sample after increasing cooling times. The concentrations were calculated using the in-house program K$_o$LABSUE, written in Turbo Pascal. This is a quasi independent data format package for k$_0$-quantification [9] based on the method developed by [10]. Gold monitors were used for short irradiations and iron and zirconium monitors for long irradiations

4 Inductively coupled plasma mass spectrometry (ICP-MS)

ICP-MS as a method for inorganic trace analysis shows an excellent sensitivity for a large number of elements of interest and the speed of measurement makes it suitable for routine, multielement determinations at trace and ultra trace levels. However environmental studies require determination of the total content of the sample, not just the more soluble part. Solid samples must be dissolved prior to ICP-MS analysis, which may be the most difficult part of the analysis. Losses and contamination have to be avoided. However, the sample solution should have a total dissolved solid content of not more than 0.1% to avoid signal depression and drift. Matrix effects on ICP-MS trace determinations have been extensively discussed in the literature [11,12,13]. Isobaric interferences on the analyte masses due to isotopes of other elements can be easily taken into account. Corrections of interferences due to the formation of ions of oxides, hydroxides and other diatomic species depend on the matrix and instrumental conditions.

Different methods for the total dissolution of biological materials [4] have been tested in closed and open systems

The muscle, gills, digestive glands and carapace samples (about 50 g in size) were digested to the Teflon closed digestion bombs in the microwave (ETHOS PLUS) using the super analytical reagent grade of following sequence: 4 ml HNO_3 + 1 ml HC1 .

The ICP-MS instrument used was the PQ Excell from VG Elemental , Service Central d'Analyse – CNRS, Lyon, France. The instrument settings and operating conditions are shown in Table 2. Signal drift due to matrix effects was monitored by adding internal standards (In, $10\mu g.l^{-1}$) to sample and standard solutions.

Table 2. ICP-MS operating conditions – Service Central d'Analyse Laboratory.

Instrument	PQ Excell from Elemental
Plasma gas	Argon
Fonvard/Reflected power	1350 W
Nebulizer gas flow	0.8 1 min^{-1}
Cooland gas flow	13.5 l min^{-1}
Spray chamber Peltier-cooled	3 ˚C
Interface Interface pressure	1.7 mbar
Auxiliary gas flow	0.7 l/min
Analyser pressure	8-10 mbar

5   Results and discussion

The analytical methods were tested on several international CRM, mainly those distributed by the International Agency of Atomic Energy in Vienna (IAEA). We used: Soil-7 for soils and SLRS-3 (River water reference material for trace metals, distributed by the National Research Council of Canada) for water.

Table 3 and 4 show the results obtained by INAA and ICP-MS for Soil-7 and SLRS-3, table 5 and 6 show the results of four type organs the different crustaceans. Most of the values obtained by INAA and ICP-MS agreed with the certified values. These analyses of reference samples were used to specify the best method for each of the elements of interest in our study. The choice was based on the reliability of the result and practical features. For example, a method could give good results but requires sample preparation inadequate for the number of samples to be treated. The choice of method also depended on the form of the material analyzed. For soil, sediment and plant, INAA had the great advantage of not requiring dissolved samples. ICP-MS requires dissolved samples, with non-negligible risk of pollution and loss. Some metal oxides were sometimes incompletely dissolved because all chemicals could not be used (e.g. memory effects due to the use of alkaline fusion). Table 7 summarizes the reasons for analyzing each element.

The elements Cu, Pb, Nb and Y were accurately determined by ICP-MS, while their determination by INAA was impossible or difficult. They gave no usable radionuclide or sensitivity was poor, demanding time-consuming chemical separation before measuring radioactivity. The elements Cr, Co, were accurately determined by the two methods. But their peaks were disturbed by more abundant neighboring elements in ICP-MS measurements. The INAA results were generally used because of their high neutron activation cross section and well differentiated gamma rays. The elements Al, Mg and Ti were measured by INAA using a short-life radionuclide requiring a short irradiation. The abundance of Al and Na giving ^{28}A1 ($T_{1/2}$ = 2.24 min) and ^{24}Na ($T_{1/2}$= 4.96 h) occasionally concealed less abundant elements (Mg and Ti). ICP-MS seemed to be preferable, provided that the Ti and Al oxides were completely dissolved and a suitable dilution was used. Isobaric interference on ^{40}Ar and ^{40}Ar^{16}O prevented the use of the most abundant isotopes of the major elements, Ca and Fe in ICP-MS, although the sensitivity of INAA for Fe and Ca was poor. They were determined by both methods if they were in high concentration. The Fe concentration was confirmed by the ^{54}Fe(n,p)^{54}Mn reaction induced by epithermal neutrons.

The elements Cr, Co and Ni may all be contaminated during the dissolution needed for ICP-MS, and ^{40}Ar^{12}C and ^{40}Ar^{12}C^{1}H interfered in Cr determinations. Cr and Co were accurately determined by INAA (high cross section and well identified gamma-rays). INAA was not very sensitive to Ni determination using the [5] reaction: low concentrations required the use of the reaction ^{58}Ni(n,p)^{58}Co with epithermal neutrons. Arsenic was readily determined by both methods, but there were risks of losses during the dissolution of solid samples prior to ICP-MS. INAA was more accurate than ICP-MS but less sensitive. Sr and Ba were easily assayed by ICP-MS, while for INAA, the gamma-rays of the radio-nuclides used were badly differentiated at low concentrations.

The uranium fission has to be considered in INAA determinations of elements having and atomic weight between 95 and 140, mainly Zr [14]

The rare earth elements (La ,Ce) we readily assayed by the two methods. La and Ce assays suffered from interference with uranium fission, but only in uraniferous rocks. We used INAA to assay these elements. The detection limit of some elements could be reduced in INAA using an anti-Compton system [15].

6   Conclusions

Both INAA and ICP-MS methods are suitable for studying the main mineral elements in pollution studies. They have practically the same sensitivity, with a far greater dispersion from an element to the other in the case of INAA. ICP-MS has many advantages over INAA: it is much faster, requires no radioactivity and can determine simultaneously more elements. The greater drawbacks of INAA for environmental studies are the low sample throughput, the production of radioactive waste and the impossibility to measure lead, one of the most widely measured elements. But ICP-MS appears to be generally less accurate than INAA. There are more sources of error than in INAA (sample preparation, isobaric interferences, signal drift). The ideal method would be to combine both approaches, with ICP-MS being used for routine analyses, and INAA reserved for developing analytical procedures, control analyses and for difficult to dissolve substrates or elements having strong mass interference. But the use of NAA depends on access to an experimental nuclear reactor, and unfortunately the number of these facilities in the world is decreasing.

Table 3. Results obtained by INAA and ICP-MS - SLRS-3 (in $\mu g.l^{-1}$)

Element	Concentrations measured ± standard deviation		Certified concentrations (conf limits range)	
	INAA	ICP-MS		
Mg		1430 ± 100		
Al		29 + 3	31*	28-34
Ca	5700 ± 600	5900 ± 600	6000	5600-6400
Ti		1.0 ± 0.1		
Cr	0.38 ± 0.04	0.38 ± 0.04	0.30*	0.26-0.34
Fe	110 ± 10	103 ± 20	100	98-102
Co	0.042 ± 0.004	0.04 ± 0.1	0.027	0.024-0.030
Ni		0.9 + 01	0.83	0.79-0.91
Cu		1.5 ± 0.2	1.35	1.28-1.42
As	0.67 ± 0.07	0.70 ± 0.1	0.72	0.67-0.77
Rb	1.75 + 0.18	1.7 ± 0.1	1.72	1.52-1.92
Sr	32 + 3	29 + 2	28.1*	
Y		0.13 + 0.02		
Cd		<0.02	0.013	0.011-0.015
Sb	0.17 ± 0.02	0.14 ± 0.04	0.12	0.11-0.14
Ba	14 ± 2	13.0 + 0.6	13.4*	12.8-14.0
Pb		0.08 ± 0.05	0.068*	0.061-0.075
Th	0.017 ± 0.002	<0.02		
La	0.26 ± 0.03	0.26 + 0.02		
Ce	0.33 ± 0.03	0.30 + 0.03		

* Information values only

Table 4. Results obtained by INAA and ICP-MS - Soil 7 -IAEA (in $\mu g.g^{-1}$)

Element	Concentrations measured ± standard deviation		Certified concentrations (conf limits range)
	INAA	ICP-MS	
Mg		11900±500	11300* (11000-11800)
Al		66550±2000	47000* (44000-5 1000)
Ca	164000±16400	145000±15000	163000* (157000-174000)
Ti		2100±200	3000* (2600-3700)
Cr	63±6	63±2	60 (49-74)
Fe	25700±2000	25000±1000	25700* (25200-26300)
Co	8.6±0.8	10.5±1.0	8.9(8.4-10.1)
Ni		38±8	26* (21-37)
Cu		13±2	11(9-13)
As	13.3±1.3	14.8±1.2	13.4(12.5-14.2)
Rb	49±5	53±1	51 (47-56)
Sr		108±1	108(103-114)
Y		16±2	21(15-27)
Cd		l.6±0.2	1.3* (1.1-2. 7)
Sb	1.8±0.2	1.6±0.1	1.7(1.4-1.8)
Cs	5.5±0.5	5.7±0.1	5.4(4.9-6.4)
Ba	141±20	138±2	159* (131-196)
Pb		59±2	60(55-71)
Th	8.1±0.8	8.0±0.2	8.2(6.5-8.7)
Ce	58±6	55±1	61 (50-63)
* Information values only			

Table 5. Results for the crustaceans (Macrobrachium carcinus) by ICP-MS and INAA (μg/g)

Element	Digestive Glands		Carapace		Muscle		Gills	
	ICP-MS	INAA	ICP-MS	INAA	ICP-MS	INAA	ICP-MS	INAA
Mg(2)	1596±160		127±13		935±95		1668±162	
Al(2)	26±5.0		111±20		10±2.0		376±65	
Ca(2)	168531± 17000	155323± 15000	491151± 49000	457231± 45000	96288± 9600	91543± 9100	33419± 3000	32835± 32000
Ti(2)	23±0.21		185±14		2.2±0.2		30±3.0	
Cr(1)	326±33	283±30	53±5.0	49±5.0	40±4.0	38±3.8	77±8.0	69±7.0
Fe(1)	6811±500	621±65	1806±180	1765±10	284±28	275±28	1100±100	1020±100
Co(1)	0.23±0.03	0.21±0.02	1.6±0.16	0.13±0.1	0.23±0.3	0.22±0.2	1.0±0.1	0.9±0.09
Ni(2)	4.1±0.8	<5	14	10±5	5.7±1.1	<7	12±2.4	9±2.0
Cu(2)	351±50		101±15		80±12		252±30	
As(1)	5.3±0.6	4.8±0.5	4.5±0.5	4.0±0.4	0.58±0.6	0.52±0.5	3.0±0.3	2.7±0.27
Rb(2)	5.4±0.6	5.0±0.5	0.64±0.6	0.61±0.6	0.95±0.1	0.92±0.1	1.5±0.15	1.2±0.12
Sr(2)	414±42		862±87		60±6.0		226±23	
Y(2)	0.1±0.03						0.50±0.15	
Ag(2)			0.37±0.04	0.33±0.034	0.14±0.012	0.12±0.02	0.6±0.06.	0.53±0.05
Cd(2)	0.4±0.04	0.37 ±0.04	0.22±0.02	0.18±0.02	<0.2	<0.1		
Ba(2)	9±0.9	8±0.8	162±16	155±13	22±2.0	20±1.9	27±2.2	25±2.6
Pb(2)	1.5±0.15		1.3±0.13		3.2±0.32		3.7±0.4	
La(1)	0.4±0.04	0.38±0.04	0.44±0.04	0.42±0.04	<0.08	<0.1	1.8±0.15	1.6±0.15
Ce(1)	0.6±0.06	0.58±0.05	0.52±0.05	0.55±0.05	<0.07	<0.05	2.8±0.2	2.6±0.2

Recommended method: (1) INAA (2) ICP-MS

Table 6. Results for the crustaceans(Ucides cordatus) by INAA and ICP-MS (μg/g)

Element	Digestive Glands		Carapace		Muscle		Gills	
	ICP-MS	INAA	ICP-MS	INAA	ICP-MS	INAA	ICP-MS	INAA
Mg(2)	593±55		7000±560		2434±225		1286±112	
Al(2)	100±20.		145±22		274±51		5273±108	
Ca(2)	105538± 10000	98556± 9000	1094960± 100000	995437± 98000	207951± 20000	201343± 21000	106641± 10000	101322± 11000
Ti(2)	3.0±0.29		12±1.4		12±1.2		229±30	
Cr(1)	11±1.0	9.0±1.3	9.3±0.9	8.4±0.8	26±2.6	23±2.6	33±3.3	30±3.0
Fe(1)	717±70	688±65	21162±220	19212±190	3248±290	2975±280	3800±400	3685±380
Co(1)	0.68±0.06	0.63±0.06	3.7±0.36	3.3±0.3	1.1±0.11	0.95±0.096	2.3±0.1	2.1±0.21
Ni(2)	11±1.0	10±1.3	73±7.0	71±7.0	19±1.9	17±1.7	2.3±0.23	2.2±0.22
Cu(2)	12±1.0		43±4.0		51±5.1		48±5.0	
As(1)	1.8±0.18	1.6±.0.16	4.1±0.5	3.9±0.4	2.2±0.2	2.0±0.2	5.5±0.5	5.1±0.55
Rb(2)	0.47±0.05	0.43±0.05	1.2±0.12	1.0±0.1	1.9±0.19	1.6±0.16	6.3±0.63	6.1±0.63
Sr(2)	144±14		2940±290		313±31		170±18	
Y(2)	0.25±0.02		0.76±0.07		0.16±0.02		2.3±0.23	
Zr(2)		0.43±004		<0.05		0.14±0.02		3.1±0.3
Ag(2)	30±3.0	26±5.0	4.3±0.43	4.0±0.8	8.6±0.86	8.0±0.9	19±2.0	14±3.0
Cd(2)	1.5±0.2	1.2±0.3	0.91±0.1	0.8±0.1	<0.60	<0.30	2.7±0.3	2.1±0.7
Ba(2)	260±30	252±25	960±96	898±90	18±2.0	16±1.6	138±14	129±13
Pb(2)	9.8±0.9		3.2±0.3		1.9±0.02		6.2±0.6	
La(1)	0.8±0.06	0.75±0.07	2.2±0.2	2.1±0.2	0.24±0.02	0.26±0.03	8.7±0.8	8.5±0.8
Ce(1)	1.3±0.1	1.1±0.1	4.7±0.4	4.3±0.4	0.43±0.04	0.46±0.04	16±1.5	15±1.5

Recommended method: (1) INAA (2) ICP-MS

Table 7. Comparison of INAA and ICP-MS for the determination of elements

Y, Nb, Pb	ICP-MS	INAA not applicable
Mg, Al, Ti,	INAA and ICP-MS	Short time irradiation required for INAA Oxide dissolution (Al_2O_3) difficult for ICP-MS
Ca	INAA and ICP-MS	Poor sensitivity by INAA: y-ray at 1297 keV interferes with The rays of ^{59}Fe, ^{60}Co, ^{182}Ta
Cr, Fe	INAA and ICP-MS	Oxide dissolution difficult and mass interference for ICP-MS
Ni	ICP-MS	Poor sensitivity using (n,y) reaction. Better results obtained by (n,p) reaction which requires a special irradiation
Cu	ICP-MS	Poor sensitivity in INAA. Radiochemical separation required
As	INAA and ICP-MS	Loss risks during the dissolution in ICP-MS
Rb, Ag	INAA and ICP-MS	
Sr	ICP-MS	Poor selectivity of 514 keV y-ray in INAA
Cd	INAA and ICP-MS	Poor sensitivity in INAA
Co	INAA and ICP-MS	Determination accurate and sensitive by INAA
Ba	INAA and ICP-MS	Poor selectivity of 496 keV y-ray in INAA
La. Ce	INAA and ICP-MS	Interference risk with uranium fission in INAA

References

[1] M. Huynh, F. Carrot, S. Ngoc, V. MD and G. Revel, *Determination of rare earth elements in rice by INAA and ICP-MS*, Journal Of Radioanalytical and Nuclear Chemistry, 1997. 217: 95-99.

[2] M. Khalis, A. Sekkaki, J. Irigaray, F. Carrot and G. Revel, *Environmental control of Boufekrane river water basins by neutron activation analysis and ICP/MS*, Water Research, 1997. 31: 2930-2934.

[3] M. Veado, G. Pinte, A. Oliveira and G. Revel, *Application of instrumental neutron activation analysis and inductively coupled plasma-mass spectrometry to studying the river pollution in the State of Minas Gerais*, Journal of Radioanalytical and Nuclear Chemistry, 1997. 217: 101-106.

[4] M. I. G. Severo, *Etude de l'impact toxicologique des polluants minéraux (Cu, Cr) engendré par des rejets agricoles sur les crustacés de l'état de Bahia-Brésil*, Thèse Université Reims Champagne-Ardenne, 1999.

[5] L. Galsomies, M. Letrouit, C. Deschamps, D. Savanne and M. Avnaim, *Atmospheric metal deposition in France: initial results on moss calibration from the 1996 biomonitoring*, Science of the Total Environment, 1999. 232: 39-47.

[6] M. Grasso, R. Clochiatti, F. Carrot, C. Deschamps and F. Vurro, *Lichens as bioindicators in volcanic areas: Mt. Etna and Vulcano Island (Italy)*, Environmental Geology, 1999. 37: 207-217.

[7] E. Steinnes, A. Ruhling, H. Lippo and A. Makinen,, *Reference materials for large-scale metal deposition surveys*, Accreditation and Quality Assurance, 1997. 2 : 39-247.

[8] B. Market, *Sampling and Sample Pretreatment*, in P. Quevauvillier, ed., *Quality Assurance in Environmental Monitoring*, VCH, Weinheim, New York, Tokyo, 1995: 215-218.

[9] D. Piccot, C. Deschamps, R. Delmas and G. Revel, *Ko-LABSUE: A quasi non-dependent data format package for Ko quantification*, Journal of Radioanalytical and Nuclear Chemistry, 1997. 215: 263-269.

[10] F. De Corte, *The k0 - standardization method; A move to the optimization of neutron activation analysis, Ryksuniversiteit Gent*, Faculteit Van de Wetenschappen, 1986: 464 - 470.

[11] J. Cook, M. Gardner, A. Griffths, M. Jessep, J. Ravenscroft and R. Yates, *The comparability of sample digestion techniques for the determination of metals in sediments*, Marine Pollution Bulletin, 1977. 34: 537-544.

[12] I. Rodushkin, T. Ruth and A. Huhtasaari, *Comparison of two digestion methods for elemental determinations in plant material by ICP techniques*, Analytica Chimica Acta, 1999. 378:191-200.

[13] S. Wu, X. Feng and A. Wittmeier, *Microwave digestion of plant and grain reference materials in nitric acid or a mixture of nitric acid and hydrogen peroxide for the determination of multi-elements by inductively coupled plasma mass spectrometry*, Journal of Analytical Atomic Spectrometry, 1997. 12: 637-644

[14] G. Revel, *Trace and Ultratrace Analysis Accuracy in Activation-Analysis*, Analysis, 1984. 12: 506-513.

[15] S. Landsberger, *Compton Suppression Neutron-Activation Methods in Environmental Analysis*, Journal of Radioanalytical and Nuclear Chemistry, 1994. 179: 67-79.