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NEUTRON ACTIVATION ANALYSIS IN TRACE ELEMENT MEASUREMENTS ON MARINE ENVIRONMENTAL SAMPLE (MYTILUS GALLOPROVINCIALIS, MA-M-2/TM - REFERENCE MATERIAL)

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Introduction. This work presents the results regarding an intercomparison organized by the IAEA (Laboratory of Marine Radioactivity - Monaco) on the determination of trace elements in mussel tissues in order to provide a biological reference material for multielement analyses and also to verify the performance of the various analysis methods of the participating laboratories.

It is well known that mollusca are able to concentrate micropollutants in their tissues from the surrounding sea water and therefore can be considered as good indicators of heavy metal pollution of the marine environment.

The Mediterranean mussels - Mytilus galloprovincialis have been analyzed.

Experimental. By using the instrumental neutron activation method the concentration of 28 elements have been determined after a long and short irradiation in a VVRS-1 reactor. A multi channel analyser connected to a 65 cm^3 Ge(Li) detector with 2 keV resolution has been used.

Results and Discussion. In Table 1 are presented the concentration values of certified elements with satisfactory (A) or acceptable(B) degree of confidence.

As regards our results for Hg concentration a small comment is necessary. The (2.45±0.58)$\mu g.g^{-1}$ value initially obtained was rejected. We suspect a contamination in our first measurements because a $HgCl_2$ solution has been used as standard. Making use by the monostandard method this element has been reanalysed. Our value for Hg concentration (1.03±0.11)$\mu g.g^{-1}$ is in a good agreement with the recommended value. In this case we have a good reason to explain our first discrepancy and to improve the method of analysis for this element. In Table 2 the information value for the concentrations of some element are given. Table 3 presents the meaningless values, which cannot be recommended due to the limited number of participating laboratories or due to the large discrepancy of the values obtained by different methods used. A new revised analysis of Al and V has been performed in our laboratory. The value of (191±20)$\mu g.g^{-1}$ was obtained for Al concentration. For V only an upper level < 3 $\mu g.g^{-1}$ of concentration has been determined. In Table 3 we put the old values in brackets.

Finally, as one can see from tables 1,2 our results are in a good enough agreement with the certified values.

TABLE 1. Concentration values of elements that can be certified with satisfactory (Class A) or acceptable (Class B) degree of confidence

Element	Unit	Concentration	Confidence interval	Our results	Class of results
As	$\mu g.g^{-1}$	12.8	11.8-14.4	10.0±1.9	A
Br	$\mu g.g^{-1}$	357.8	304.1-416.7	353±20	A
Ca	$mg.g^{-1}$	14.8	13.6- 16.1	15.6±1.5	B
Co	$\mu g.g^{-1}$	0.88	0.75-1.07	0.91±0.01	B
Cr	$\mu g.g^{-1}$	1.25	0.95-1.62	1.17±0.09	B
Fe	$\mu g.g^{-1}$	256.2	229.2-268.2	270±17	B
Hg	$\mu g.g^{-1}$	0.95	0.85-1.06	1.03±0.11	A
Mg	$mg.g^{-1}$	5.94	5.22-6.70	5.9 ±0.4	B
Mn	$\mu g.g^{-1}$	67.1	60.7-75.3	60.8±6.5	B
Na	$mg.g^{-1}$	45.5	44.0-47.7	43.6±1.0	B
Rb	$\mu g.g^{-1}$	6.96	5.30-7.80	7.2±0.6	B
Se	$\mu g.g^{-1}$	2.27	1.70-2.56	2.0±0.1	B
Sr	$\mu g.g^{-1}$	101.3	91.5-106.7	104±6	B
Zn	$\mu g.g^{-1}$	156.5	152.8-166.7	152.3±2.7	B

TABLE 2. Information values (non-certified) for concentration of elements

Element	Unit	Concentration	Confidence interval	Our results
Ag	$ng.g^{-1}$	54.2	45.1-62.0	< 80
Au	$ng.g^{-1}$	15.5	14.4-16.3	15.5 ± 1.9
Sb	$ng.g^{-1}$	27.0	26.6-29.5	29.5 ± 4.9
Sc	$ng.g^{-1}$	45.1	42.2-48.0	42.3± 1.5

TABLE 3. Concentration values of certain non certified elements, determined in our laboratory

Element	Unit	Concentration		Number of participating laboratories
Al	$\mu g.g^{-1}$	191 ± 20	(319±13)	7
Ce	$\mu g.g^{-1}$	0.67 ± 0.06		2
Cs	$ng.g^{-1}$	76 ± 7		2
Eu	$ng.g^{-1}$	7.6 ± 1.5		3
Hf	$ng.g^{-1}$	≤ 50		2
La	$\mu g.g^{-1}$	0.80 ± 0.08		2
Ta	$ng.g^{-1}$	4.9 ± 1.6		1
Te	$\mu g.g^{-1}$	1.6 ± 0.7		1
Th	$ng.g^{-1}$	45 ± 12		2
V	$\mu g.g^{-1}$	≤ 3	(3.6±1.4)	10

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INSTRUMENTAL NEUTRON ACTIVATION ANALYSIS OF SOME SAMPLES OF AIN-FRANIN GEOTHERMAL WATER, ALGERIA

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Summary. Samples of sea water, AIN-FRANIN geothermal filtered and non filtered water,as well as a sediment rock surrounding this source were collected. Samples and standards were irradiated and counted using a Ge(Li) detector. Total of 22 elements have been identified: Na,Rb,Cs,Br,Ca,Sr,Ba,Sc,Cr,Fe,Co,Zn,As,Ag,La,Ce,Sm,Nd,Eu,Hf,Hg,U.

Material and Methods. Non filtered sewater, filtered and non filtered AIN-FRANIN water samples were evaporated and dryed at 180°C. The white crushing rock surrounding the source was also dryed at the same temperature. After crushing the samples in an agath mortar, they were together with the standards irradiated for 76 hours in a $1.1x10^{11}$ neutrons/cm^2.s flux. Making use of a high resolution Ge(Li) detector,the elements identified, are to be seen in Table 1: Na,Rb,Cs,Br,Ca,Sr,Ba, Sc,Cr,Fe,Co,Zn,As,Ag,Hg,La,Ce,Sm,Nd,Eu,Hf,U.

Conclusions: AIN-FRANIN geothermal water, has higher concentration in Sr,Sc,Fe,Zn,Cs, than in seawater. The following elements were present only in A-Fr water: Cr,Co,Ag,Hf,Hg. Arsenium was present only in marine water and in the rock surrounding the thermal source, but lack in the seawater few Km along the sea at Kristel(1). The presence of Uranium signaled for the first time at Kristel in 1984(2), now it is confirmed its origins in the geothermal source of Ain-Franin. Zn presence 60-70 µg/l at A-Fr and 22µg/l in the seawater, has not been detected at Kristel, few Km along the coast (1).

Natural Uranium has been detected in concentration of 30 µg/l in the seawater, while at A-Fr source only 2.3 µg/l. This can be explained by the accumulation of U little by little in front of deversing the source in seawater and the impossibility to diffuse more quickly in the surface or the deep layers.

TABLE 1

Element	Sample	marine water 40.24 g/ℓ nonfiltered	filtered water AIN-FRANIN 5.411 g/ℓ	nonfiltered water AIN-FRANIN 5.415 g/ℓ	Rock
Na	g/ℓ	13.61±0.16	0.80±0.02	0.88±0.02	(31.5±1.3)ppm
Rb	µg/ℓ	80 ± 8	32 ± 3	32 ± 5	-
Cs	µg/ℓ	0.5 ± 0.1	12.1±0.4	12.4±0.5	(9 ± 3) ppb
Br	mg/ℓ	15.5 ± 0.7	1.36±0.06	1.44±0.07	(0.24±0.02)ppm
Ca	g/ℓ	0.61 ± 0.06	0.832±0.026	0.786±0.023	(31.1±0.7) %
Sr	mg/ℓ	0.4 ± 0.1	9.1 ± 1.0	9.3 ± 1.0	(1861±190) ppm
Ba	µg/ℓ	< 296	-	86 ± 40	(2.3±1.4) ppm
Sc	µg/ℓ	0.02±0.06	0.08±0.03	0.44±0.04	(5.4±0.5) ppb
Cr	µg/ℓ	-	2.3 ± 0.5	8.2 ± 0.8	-
Fe	mg/ℓ	0.48±0.20	0.14±0.03	3.38±0.15	(355± 15) ppm
Co	µg/ℓ	-	0.05±0.03	0.07±0.03	(9±3) ppb
Zn	µg/ℓ	22 ± 4	60 ± 3	70 ± 3	(3.1±0.1) ppm
As	µg/ℓ	55 ± 34	-	-	(0.24±0.10)ppm
Ag	µg/ℓ	-	0.16±0.09	0.27±0.08	-
La	µg/ℓ	4.7 ± 1.7	3.8 ± 0.5	4.1 ± 0.6	(30 ± 5) ppb
Ce	µg/ℓ	3.8 ± 1.7	0.5 ± 0.3	0.7 ± 0.3	(60 ± 40) ppb
Sm	µg/ℓ	< 0.84	0.07±0.04	0.08±0.04	(45 ± 6) ppb
Nd	ppm	-	-	-	(0.6±0.3)ppm
Eu	ppb	-	-	-	< 4 ppb
Hf	µg/ℓ	-	0.07±0.04	< 0.16	-
Hg	µg/ℓ	-	0.6 ± 0.1	1.2 ± 0.2	-
U	µg/ℓ	30 ± 15	1.8 ± 0.8	2.3 ± 1.0	(0.42±0.15)ppm

The white rock principaly is made of $CaSO_4$ about 98% with a low mineralization in Sr,Fe,Ba, lanthanides and 0.42 ppm Uranium.

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