INAA of trace elements in marine sediment (SD-M-2/TM, Reference Material)

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Abstract

Determination by instrumental neutron activation analysis method of concentration of 41 elements in Mediterranean deep-sea sediment as "total" sample analysis as well as of 24 elements in partial digested sample has been performed.

Introduction

Trace elements analysis of marine sediments is an important problem from geochemical and environmental pollution studies point a view. This paper represent our contribution to the intercomparison run organized by the Marine Environment Laboratory of IAEA on trace element measurements of deep-sea sediment, as reference material, 121 laboratories from 51 countries have participated in this exercise and reported results for 62 elements, this intercomparison appears to be the widest one. The sediment sample was collected in July 1987 in the Mediterranean sea at a depth of 1240 meters.

Experimental

The samples and standards have been irradiated for long and short time in VVR-S reactor at 10^{11} - $3 \cdot 10^{12} n \cdot cm^{-2} s^{-1}$ flux. The measurements of gamma spectra have been made using a high resolution HPGe detector connected to the multichannel analyzer. Besides the "total" sample investigation, the analysis of simple partial extraction with IM hydrochloric acid has been performed in order to evaluate the effectiveness of different procedures for sample digestion.

Results and discussion

Our concentration values representing the arithmetic means of three separate determinations with the corresponding standard deviations are shown in Tables 1, 2 for total sample analysis (41 elements) and in Tables 3, 4 for partial digested sample (24 elements). A very hard and careful analysis for so many elements has been carried out in our laboratory. It is therefore a great satisfaction to have now the opportunity to pointed out the good or very good quality of our results on this valuable and convenient reference material for the future analyses.

Table 2.- Noncertified values of elemental concentrations in the marine sediment (SD-M-2/TM, reference material)

Element	Range of submitted means	Our values	Number of participated laborat.
Au (ppb)	6 - 110	6 ± 2	2
Cl (%)	1.560 - 1.566	1.566 ± 0.026	2
Dy (ppm)	1.68 - 3.83	2.97 ± 0.21	4
I (ppm)	34.7 - 77.0	34.7 ± 2.1	2
In (ppm)	0.133 - 69.50	0.133 ± 0.025	2
Mo (ppm)	2.70 - 3.43	3.43 ± 0.06	2
W (ppm)	1.7 - 2.4	2.4 ± 0.1	2

Table 3.- Elemental concentrations in partial digested marine sediment (SD-M-2/TM/P)

Element	Concentration	Confidence interval	Range of accepted results	Our values
Al (%)	0.32	0.204 - 0.408	0.18 - 0.56	0.344 ± 0.036
Ba (ppm)	35.9	27.3 - 41.7	27.3 - 41.7	37 ∓ 8
Ca (%)	12.3	10.6 - 13.9	10.6 - 13.9	13.9 ± 0.6
Co (ppm)	7.10	6.36 - 8.57	3.75 - 18.9	6.57 ± 0.64
Cr (ppm)	9.92	9.10 - 12.0	2.95 - 26.07	9.17 ± 0.46
Eu (ppm)	0.365	-	0.27 - 0.57	0.57 ± 0.06
Fe (%)	0.5136	0.430 - 0.618	0.085- 1.210	0.705 ± 0.041
K (%)	0.1565	-	0.1384- 0.1655	0.1655 ± 0.0119
La (ppm)	5.95	2.90 - 10.30	2.90 - 10.30	6.4 ± 0.5
Mn (ppm)	1003	960 - 1040	582 - 1430	946 ± 161
Na (%)	1.03	1.00 - 1.09	1.00 - 1.09	1.05 ± 0.02
Rb (ppm)	7.05	-	2.4 - 9.6	5.8 ± 0.5
Sb (ppb)	170	80 - 400	80 - 400	80 ± 3
Sr (ppm)	490	440 - 525	435 - 586	493 ± 9
V (ppm)	15.70	13.8 - 18.6	12.0 - 22.3	13.3 ± 2.3
Zn (ppm)	25.0	23.4 - 30.3	4.6 - 55.5	22.0 ± 4.4

Table 4.- Range of elemental concentrations in partial digested marine sediment (SD-M-2/TM/P)

Element	Range of submitted lab. means	Our values	Number of participated laboratories
Ce (ppm)	5.6 - 36.3	16.3 ± 1.3	5
Lu (ppm)	0.03 - 0.08	0.08 ± 0.01	3
Sc (ppm)	0.48 - 1.39	0.87 ± 0.03	6
Sm (ppm)	1.0 - 2.2	2.2 ± 0.2	4
Tb (ppm)	0.19 - 0.36	0.23 ± 0.02	3
Th (ppm)	0.23 - 0.42	0.42 ± 0.05	3
Yb (ppm)	0.35 - 0.74	0.74 ± 0.09	4
Zr (ppm)	-	27.7 ± 3.2	1

Heavy metals in seawater and surface sediments of the Gulf of Bourgas

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The Gulf of Bourgas is one of the highly polluted regions of the Black sea coasts. The pollutants includes petroleum products as well as heavy metals. The pollution is due to the geomorphological characteristics of the gulf as well as the presence of a large number of chemical industries in the vicinity of the sea. The investigations on the heavy metal present in the sea-water and the surface sediment is rather scarce. Therefore such a study is very interesting from the analytical as well as ecological viewpoint.

In May and September 1991, an average sample was done simultaneously from the sea water and the surface sediment at three different stations : namely Bourgas Port (I), Petroleum Port (II) and the bulk of the gulf (III). The samples were analysed by suitable electroanalytical methods.

The sediments were collected from the surface by a conventional apparatus, dried at a temperature of 105°C, grinded and fractioned. The preweighed dry sample (d < 0.06 mm) was dissolved in HCl (2:1) on heating, filtered out and analysed by polarographic method with standard deviation [1]. The completeness of the extraction process was controlled by the atomic emission spectral analysis of the insoluble residue.

The Pb content was determined directly in the filtrate. A part of the solution was evaporated to complete drying, then dissolved in excess NH_3 and filtered again. Cu, Zn and Cd contents were determined simultaneously by the polarographic method.

The samples from the sea water was collected in plastic bottles pretreated with HNO_3 and filtered through a membrane filter (pore-diameter < 0.45 μ). With a view to eliminate the organic impurities, the samples were subjected to electrochemical anodic oxidation at +1.4 V for 10 min in a graphite container.

The mentioned heavy metals in the sea-water were determined by a method of anodic stripping voltametry (ASV) [2] under the following conditions: stripping process on HMDE at 1.2V vs SCE for 10 min, deoxidation with N_2 and anodic dissolution of the deposited impurities at a rate of 400 mV/min. The metals under investigation show well-defined sigle peaks and their concentrations were determined by a method of standard addition.

Table 1

Heavy metals in sea-water (sw), μg/l and sediments (sed) μg/g dw

Station		Cu		Zn		Cd		Pb	
		V	IX	V	IX	V	IX	V	IX
I	sw	10.3	11.2	9.3	9.9	0.25	0.23	0.05	0.05
	sed	93.4	99.9	52.4	53.3	3.70	3.90	73.40	78.80
II	sw	15.1	16.8	10.4	10.5	0.28	0.30	0.06	0.07
	sed	115.2	107.6	53.3	61.4	4.80	4.70	79.50	78.10
III	sw	8.7	9.1	10.1	12.0	0.21	0.23	0.04	0.07
	sed	82.2	82.1	50.8	52.2	3.60	3.70	70.40	73.30

The experimental results show that the concentrations of Cu and Cd at station II are the highest - a fact most probably attributed to the presence of Copper mine nearby. The Pb concentrations is comparatively higher at the stations I & II, however Zn concentration is almost constant. Although no general conclutions can be drawn for the seasonal changes in the heavy metal contents, it may be noted that in September, their concentrations are higher. There exist some correlation between the heavy metal contents in the sediments and that in the corresponding sea-water.

The electrochemical methods proposed for the analysis of Cu, Cd, Pb & Zn are rapid, sensitive and selective. Relative standard deviation for the polarographic determination is 2-5 % and that for ASV is 8-12 % (n =6).

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