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Trace element characterization by INAA of three sediments to be certified as standard reference materials

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Abstract

Three environmental matrices proposed as Certified Reference Materials, issued by the EU Standards, Measurement and Testing Programme (SMTP) formerly Bureau Communautaire de Reference (BCR) have been characterized for their trace element contents.

The materials are: BCR 277 R Estuarine Sediment, BCR 280 R Lake Sediment and BCR 320 R Channel Sediment.

Several trace elements, including As, Co, Cr, Fe, Mn, Ni, Sb, Sc, Th, U and Zn have been determined by our laboratory using Instrumental Neutron Activation Analysis (INAA). Our contributed values are being considered for the final certification.

Keywords: Sediment; INAA; Trace element

1. Introduction

The request for accurate trace element analyses in sediments to monitor the quality of the environment has dramatically increased in the last decades. The quality of the freshwater and marine environment can be monitored by analyzing the water, but monitoring of the contents in water is not sufficient. Analysis of a water sample just allows to know the concentration at the moment of sampling [1]. The total pollution history over a longer period of time, including peak concentrations, can only be monitored by measuring the integrated contents of the sediments in equilibrium with the aquatic phase. The monitoring of heavy metal concentrations in different sediment phases is important in order to assess the capability of different binding sites to adsorb or release metals to the aquatic phase [2,3]. Only a part of the total quantity of the metals present in a sediment is involved in short-term geochemical processes and interactions and may be considered bioavailable, labile or mobile [4] [5]. Sediments are analyzed because they provide the history of the evolution of the pollution in the stratigraphic structure, useful also for the decision for the possible removal or utilization [6]. The necessity of acquiring reliable analytical results by different techniques has increased the demand for different Standard or Certified Reference Materials (SRMs or CRMs) certified for trace element contents [1,7]. The Bureau Communautaire de Reference (BCR) produced and certified since decades ago many geological Reference Materials. Among them three sediments of different origin, composition and behaviour in the dissolution and other analytical processes were issued, distributed and certified in 1988: BCR CRM 277 Estuarine Sediment, BCR CRM 280 Lake Sediment and BCR CRM 320 River Sediment. The certification was done with our laboratory's contribution.

The request of these sediments was so high that all of them were sold out. The EU Standards, Measurement and Testing Programme (SMTP) is the new EU structure devoted to Reference Materials. At the Institute for Reference Materials and Measurements (IRMM) in Geel (B), three sediments similar to the old ones are being characterized and certified. The three sediments should represent

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different concentrations in contaminants and should reflect the final results of incoming contamination from various origin.

2. Materials and methods

The new materials analyzed are: BCR 277 R Estuarine Sediment, BCR 280 R Lake Sediment and BCR 320 R Channel Sediment.

Sediments are complex mixtures of inorganic materials and metal compounds from anthropogenic sources. For the analysis of sediment samples, chemical dissolution must often be performed, but in most cases silicate and spinel minerals are not easily digested, which may cause analytical error in element determination [8].

In this work, the analytical technique employed was Instrumental Neutron Activation Analysis (INAA) using the Triga Mark II reactor (250 kW) of the University of Pavia for the activation and an ORTEC system for gamma-ray spectroscopy. INAA is a purely instrumental method which does not require any chemical treatments, including dissolution, of the samples to be analyzed, thus reducing the possibility of contamination and losses. For these new matrices, our laboratory is contributing to the certification at trace levels of As, Co, Cr, Fe, Mn, Ni, Sb, Sc, Th, U and Zn.

The irradiation and counting parameters utilized for the element analyses are reported in Table 1. Primary standards were used for the elemental evaluation and different SRMs or CRMs were employed only for verification. Both were coirradiated with samples (Table 2). In INAA, it is very important to assess possible sources of error and their reproducibility. Fig. 1 reports the uncertainty budget indicating all the possible sources of error which could affect the final results. For each element, counting statistics is the most specific and relevant.

Table 2
Primary standards and verification materials used for INAA

Element	Primary standards (SPECPURE, Johnson Matthey)	Verification materials		
		Material	Certified (mg/kg)	Found (mg/kg)
As	As_2O_3	NBS 1635	0.42±0.15	0.46±0.06
		NBS 1632a	9.3±1	9.3±0.7
Co	Co metal dissolved in HNO_3	NBS 1633a	46±2	44±2
		BCR 146R	7.39±0.27	7.34±0.15
Cr	$K_2Cr_2O_7$	NBS 1635	2.5±0.3	2.3±0.2
		NBS 1632a	34.3±1.5	34.0±1.6
Fe %	Fe_2O_3	NBS 1633a	9.40±0.10	9.48±0.15
		BCR 146R	17.7±0.5	15.82±0.14
Mn	MnO_2	NBS 1635	21.4±1.5	20.4±1.3
		NBS 1632a	28±2	29.8±2.2
Ni	Ni metal dissolved in HNO_3	NBS 1633a	127±4	120±18
		BCR 146R	69.7±4	68.3±3
Sb	Sb_2O_3	NBS 1633a	6.8±0.4	7.0±0.5
		BCR 176	412±18	412.8±21.6
Sc	Sc_2O_4	NBS 1633a	40±2	39.5±1.9
		BCR 176	4.51±0.2	4.53±0.2
Th	ThO_2	NBS 1633a	24.7±0.3	25.0±0.6
		BCR 176	11.2±0.3	10.5±0.3
U	U_3O_8	NBS 1633a	10.2±0.1	10.2±0.3
V	V_2O_5	NBS 1635	5.2±0.5	4.5±0.3
		NBS 1632a	44±3	44±3
Zn	Zn metal	NBS 1635	4.7±0.5	4.8±0.4
		NBS 1632a	28±2	28.2±2.3

3. Results and discussion

To illustrate the actual precision of the method, in Table 3, the As contents determined in six different replicates of the same sample are reported.

Table 1
Irradiation and counting parameters

Method: INAA
Spectrometer: ORTEC DSPEC
Detector: ORTEC intrinsic Ge
Resolution: 1.67 keV on 1173.24 keV ^{60}Co line

Element	Isotope	Gamma line (keV)	Irradiation flux (n cm^{-2} s^{-1})	Irradiation time	Decay time	Counting time (s)
As	^{76}As	559.10	1.2×10^{12}	10 h	48 h	3000
Co	^{60}Co	1173.24	1.2×10^{12}	10 h	30 days	20,000
Cr	^{51}Cr	320.07	1.2×10^{12}	10 h	30 days	20,000
Fe	^{59}Fe	1099.22	1.2×10^{12}	10 h	30 days	20,000
Mn	^{56}Mn	846.60	4.0×10^{12}	300 s	1 h	600
Ni	^{58}Co	810.75	1.2×10^{12}	10 h	10 days	20,000
Sb	^{124}Sb	1691.04	1.2×10^{12}	10 h	30 days	20,000
Sc	^{46}Sc	1120.52	1.2×10^{12}	10 h	30 days	20,000
Th	^{233}Pa	311.89	1.2×10^{12}	10 h	10 days	20,000
U	^{239}Np	277.60	1.2×10^{12}	10 h	3 days	5000
V	^{52}V	1434.06	4.0×10^{12}	300 s	100 s	300
Zn	^{65}Zn	1115.52	1.2×10^{12}	10 h	30 days	20,000