Instrumental Neutron Activation Analysis of Proposed Marine Sediment Reference Material (Iaea-158)

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Summary: IAEA-158, sediment prepared by the International Atomic Energy Agency - Marine Environmental Laboratory (IAEA-MEL), Monaco was received under the IAEA Analytical Quality Control Services (AQCS) Intercomparison Programme. Instrumental Neutron Activation Analysis (INAA) was used to determine Al, As, Br, Ce, Co, Cr, Cs, Eu, Fe, Hf, K, La, Lu, Mn, Na, Nd, Rb, Sb, Sc, Se, Sm, Ta, Tb, Th, V, Yb and Zn in this proposed reference material (RM). Four different irradiation protocols were adopted using a miniature neutron source reactor (MNSR) by varying the irradiation, cooling and counting times. IAEA-405 (Estuarine Sediment) and IAEA-SL1 (Lake Sediment) were used as compatible matrix reference materials for quality assurance (QA) purposes. Good agreement between our data and IAEA certified values was obtained providing confidence in the reported data.

Introduction

Reference materials play an important role in evaluating and maintaining the quality and reliability of analytical data. They are used to validate the measurement process, and hence verify the analytical performance of a laboratory. Therefore the use of reference materials (RMs) for reliable chemical analysis is an integral part of certified laboratories to maintain the accuracy and precision of their analytical results and follow the analytical quality assurance and control (QA/QC) procedures and may also assist in the improvement of analytical procedures and performance [1]. The International Organization for Standardization (ISO) Guides 32: 1997 (E) [2] and 33: 2000 (E) [3] list more comprehensive uses of reference materials for method validation and measurement uncertainty, correcting for equipment working conditions and calibration, differences among analysts and verification of the correct use of a method [4, 5]. Calibration through the use of RMs can establish traceability in chemical and analytical measurements. Quality assurance of any measurement system can therefore be achieved by the use of RMs giving essential accuracy within the measurement method [6]. For this reason a diverse inventory of well-characterized RMs for trace elements determination is required apart from primary RMs, which are synthetically prepared, as matrix RMs provide a more realistic approach for the validation of the characterized data. Such RMs also show corresponding analytical compatibility and identical interferences as the sample under investigation.[5] Many international bodies such as EURACHEM, IUPAC and ISO have made considerable efforts to establish guidelines for a general quality system to be applied in analytical laboratories to trace and document their results in such a way that compatibility between laboratories can be obtained [7, 8]. A regular independent assessment of the technical performance of a laboratory is recommended as an important means of assuring the validity of analytical measurements not only as part of an overall quality management strategy but also to demonstrate competence and provide confidence to clients and customers. For this reason regular participation in proficiency tests (PTs) and inter-laboratory comparison exercises is required. To maintain confidence in our analytical capabilities, the Neutron Activation Laboratory at the Chemistry Division, PINSTECH has been a regular participant in IAEA Analytical Quality Control Exercises [9-12]. INAA is a preferred technique that has been adopted by international organizations as a physically independent reference method for the certification of RMs and CRMs of marine origin [8, 13, 14].

Long range transport and enrichment of pollutants in sediments from estuaries is currently a

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major topic of concern due to local anthropogenic emissions from the neighbouring urban and industrial areas [15, 16]. The knowledge of abundance and distribution of trace elements provides useful information on the geochemistry of their origin and in the study of oceanographic processes [17]. Reliable and accurate data in such studies can be obtained with the help of matrix RMs. To address this problem IAEA-MEL recently launched a worldwide intercomparison exercise for the determination of trace elements in IAEA 158 sediment sample from North Channel. The NAA Laboratory at PINSTECH took part in this exercise. The results obtained at the NAA Laboratory are presented in this paper.

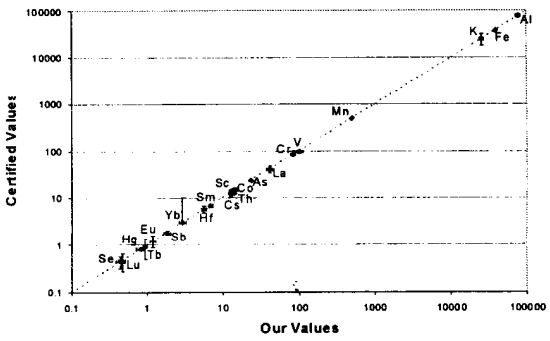

Fig. 1: Comparison of our values with certified values for IAEA SL1 (Lake Sediment).

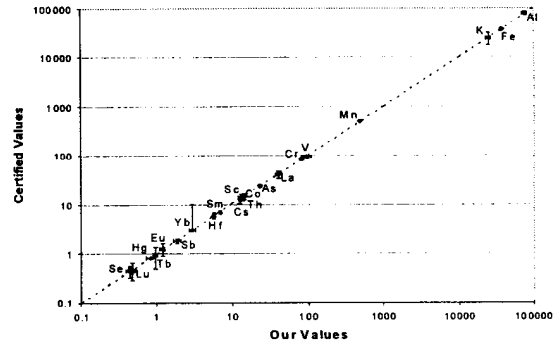

Fig. 2: Comparison of our values with certified values for IAEA-405 (Estuarine Sediment).

Results and discussion

Twenty seven trace elements have been determined in IAEA-158 (sediment) using INAA. The concentrations of all the elements reported to IAEA were corrected for the moisture content of 6.79 %. The elemental interferences for most of the elements were eliminated by variation in irradiation, cooling and counting times as given in Table-1. Nuclear interferences were found to be negligible because fast flux in MNSR type of reactor is very low. The interference of ^{28}Mg with ^{56}Mn was encountered by measuring Mn in the second counting (2m/2h/300sec) where the peak of Mn was well resolved from Mg at 843 keV. Spectral interference for the determination of ^{203}Hg in the presence of ^{75}Se was corrected as mentioned in our earlier work [18]. Peak interferences of ^{65}Zn and ^{46}Sc were corrected as mentioned elsewhere [10].

Quality assurance (QA) data were also obtained for two certified reference materials, IAEA-405 (Estuarine Sediment) and IAEA-SL1 (Lake Sediment) and are presented in Figs. 1 and 2 respectively. Fig. 1 shows that for IAEA-SL1 the difference between both data sets is generally below 10%, the exceptions being Hg, Ta and Tb. The deviation between the values for Hg is slightly above 10 % whereas the differences for Ta and Tb are ~18 and 33% respectively. The concentrations for all of these three elements are given as information values in the certificate for this CRM which implies a lower confidence in their reliability. The matrix of the proposed RM is quite similar to IAEA-405 (estuarine sediment) and it can be seen from Fig. 2 that all the trace elements were determined with % deviation of <5% between the IAEA and our results. From these plots it can be seen that the measured concentrations and reference values show no significant difference. The accuracy of our results is expected to provide an estimate of concentration with as high degree of confidence as observed in some of our previous exercises [9-12].

Elemental concentrations in IAEA-158 determined using INAA are summarized in Table-2.

Table-1: Optimum activation scheme for INAA sequential, short, intermediate and long irradiation protocols at PARR-2.

Irradiation protocol	Irradiation time/cooling time/ counting time	Isotope quantified
Sequential	2min/3min/2min	^{28}Al, ^{52}V
Short	2min/2hr/5min	^{56}Mn, ^{155}Sm
Intermediate	5hr/3days/30min	^{76}As, ^{82}Br, ^{140}La, ^{42}K, ^{24}Na
Long	5hrs/3weeks/16hr	^{141}Ce, ^{60}Co, ^{51}Cr, ^{134}Cs, ^{152}Eu, ^{59}Fe, ^{181}Hf, ^{177}Lu, ^{145}Nd, ^{86}Rb, ^{124}Sb, ^{46}Sc, ^{75}Se, ^{153}Sm, ^{177}Ta, ^{178}Tb, ^{233}Th, ^{175}Yb, ^{65}Zn

Table-2: INAA of trace element in IAEA proposed reference material IAEA-158 (Sediment)

Element/ Oxide	Mean Value (µg/g)	Uncertainty (µg/g)	Detection Limit (µg/g)	Repeatability (%)
Al	44300	3270	1220	7.4
Al_2O_3	83750	6170	2300	7.4
As	8.24	0.88	0.25	10.7
Br	215.8	19.3	114.0	8.9
Ce	63.0	3.8	1.3	6.0
Co	8.87	0.59	0.30	22.7
Cr	74.0	3.9	3.3	5.2
Cs	3.65	0.18	0.45	4.8
Eu	0.97	0.09	0.06	9.7
Fe	26080	1100	360	5.2
Fe_2O_3	37260	1570	520	5.2
Hf	5.7	0.2	0.2	4.2
K	19060	2200	3810	11.5
K_2O	22970	2650	4590	11.5
La	28.6	2.5	2.0	8.8
Lu	0.28	0.03	0.02	10.1
Mn	331.5	42.6	2.1	12.8
MnO	430	55	3	12.8
Na	23760	890	190	3.7
Na_2O	32020	1200	260	3.7
Nd	31.0	3.0	2.2	9.5
Rb	73.6	7.0	24.3	9.5
Sb	1.34	0.14	0.30	10.5
Sc	8.1	0.3	0.1	3.2
Se	0.46	0.05	0.19	11.4
Sm	4.6	0.3	0.1	5.4
Ta	0.93	0.10	0.05	10.5
Tb	0.70	0.04	0.03	6.3
Th	8.3	0.4	0.2	4.4
V	63.9	4.2	16.8	6.6
Yb	1.94	0.18	0.25	9.2
Zn	150.6	13.5	3.6	8.9

As specified by the IAEA, the concentration for each element was determined as an arithmetic mean of at least six independent determinations obtained from several irradiations. Through the optimized methodology 4 major elements (Al, Fe, K, Na), 3 minor elements (Br, Mn, Zn) and 20 trace elements (As, Ce, Co, Cr, Cs, Eu, Hf, La, Lu, Nd, Rb, Sb, Sc, Se, Sm, Ta, Tb, Th, V, Yb) were characterized in IAEA candidate sediment reference material. Mean concentration value, uncertainty, detection limit and repeatability for 27 quantified elements have been presented in this table. Limits of detection were calculated using three standard deviations as recommended by Committee of Environmental Improvement of the American Chemical Society [19]. As recommended by Eurachem/Citac Guide 2002 [20], the uncertainties in the analytical results were obtained after estimating the contribution from all sources i.e. errors in weighing, spectral peak counts, background counts and uncertainties in standard values.

The results in Table-2 include data for common oxides which occur in sediments; i.e. Al_2O_3, CaO, Fe_2O_3, KO, MnO, and Na_2O. The oxides CaO, MgO and TiO_2 were not detected in this sample whereas SiO_2 can not be determined using INAA but is a major component of sediments. The above oxides amount to around 17.64 %. The remaining elements occur in trace amounts so around 80% of the sediment is probably SiO_2. The results obtained fall well within the ranges of trace elements cited for commonly available sediment CRMs, such as lake sediment CRMs CANMET-LKSD-1 and CANMET-LKSD-1 and stream sediment CRMs GBW 07303, GBW 07304, GBW 07306 and GBW 07309 making it a suitable reference material for use in environmental, marine and geological studies. Moreover up to 27 elements including the Rare Earth Elements (REEs) Ce, Eu, La, Lu Nd, Sm, Tb and Yb have been quantified in this sample. Furthermore, it can be concluded that nondestructive, multielement and highly sensitive capabilities of INAA can be confidently used to characterize the sediment materials with relatively high precision. Our experience of analyzing such samples, the good performance of our laboratory at past international PT exercises and the QA data obtained during this study have provided us confidence in the reliability of our results. The certification of the studied IAEA sediment material from North Channel will definitely provide a useful addition to the inventory of reference material that can be used for the pollution migration studies.

Experimental

Sample Preparation

A large quantity of the sediment from North Channel was collected by IAEA-MEL. The material was dried, ground and sieved. Then it was homogenized by mixing in a stainless steel rotating drum for two weeks. Aliquots of about 20 g were packed into glass bottles with Teflon lined screw caps and sealed in plastic bags. The material homogeneity for trace elements was tested using a standard protocol and found to be satisfactory for the purpose of the intercomparison exercise (for 200 mg sub-sample) [21]. The prepared samples were distributed to laboratories around the world by IAEA-MEL for an intercomparison.

The samples were analyzed as such in our laboratory without any further processing. However each sample was handled with great care to avoid contamination and moisture absorption. About 200

mg of IAEA-158 in triplicate along with suitable matrix-based reference materials IAEA-405 (Estuarine Sediment) and IAEA- SL1 (Lake Sediment) as control materials, were packed and sealed in polyethylene capsules. Multiple batches of these samples were then packed and sealed in polyethylene rabbits for optimized irradiation.

Sample Irradiation and Counting

The sealed targets were loaded and sent for different optimized irradiation times in the Pakistan Research Reactor-II (PARR-II), which is a 27 kW, MNSR Reactor with a thermal neutron flux of $1x10^{12}$ $cm^{-2}s^{-1}$. The suitability of use of MNSR for different matrices and some practical aspects are mentioned elsewhere [22, 23]. Identical irradiation, cooling and counting protocols were adopted for the sample and the control materials as given in Table-1. The irradiated samples, after the desired cooling times, were transferred to pre-weighed fresh polyethylene capsules and counted in accordance with the optimized counting schemes using a high purity germanium detector (Canberra Model AL-30) hooked to PC-based Intertechnique Multichannel Analyzer (MCA). "Intergamma, version 5.03" software was used for data acquisition. The system has a resolution of 1.9 keV at 1332.5 keV peak of ^{60}Co and peak to Compton ratio of 40.1. The data files were subjected to calculations on our validated in-house computer programs. All necessary corrections (background subtraction etc) were applied and the final results obtained on dry weight basis. The dry weights were obtained by drying a sub-sample (not taken for analysis) at 105°C for 24 hours. Error propagation rules were applied at each stage of the calculations and accounted for the uncertainties in peak area, uncertainties in weighing and uncertainties in certified values of RMs used for quantification.

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