

INSTRUMENTAL NEUTRON ACTIVATION ANALYSIS OF MARINE SEDIMENT IN-HOUSE REFERENCE MATERIAL

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ABSTRACT

Reference materials play an important role in demonstrating the quality and reliability of analytical data. The advantage of using in-house reference materials is that they provide a relatively cheap option as compared to using certified reference material (CRM) and can closely resemble the laboratory's routine test sample. A marine sediment sample was designed as an in-house reference material, in the framework of quality assurance and control (QA/QC) program of the Neutron Activation Analysis (NAA) Laboratory at Nuclear Malaysia. The NAA technique was solely used for the homogeneity test of the marine sediment sample. The CRM of IAEA- Soil 7 and IAEA- SL1 (Lake Sediment) were applied in the analysis as compatible matrix-based reference materials for QA purposes.

ABSTRAK

Bahan rujukan memainkan peranan penting dalam memberi petunjuk kualiti dan keyakinan terhadap data analisis. Kelebihan menggunakan bahan rujukan 'in-house' adalah ia menyediakan pilihan yang lebih murah berbanding bahan rujukan pawai dan ia boleh lebih menyerupai sampel ujian rutin makmal. Satu sampel sedimen marin telah dipilih sebagai bahan rujukan 'in-house' dalam struktur program kualiti jaminan dan kawalan (QA/QC) Makmal Analisis Pengaktifan Neutron (APN) di Nuklear Malaysia. Hanya teknik APN yang digunakan untuk ujian kehomogenan sampel sedimen marin. Bahan Rujukan Piawai IAEA- Soil 7 dan IAEA- SL1 (Sedimen Tasik) telah digunakan dalam analisis ini sebagai bahan rujukan yang mempunyai matrik bersesuaian untuk tujuan kualiti jaminan.

Keywords: in-house reference material, neutron activation analysis, marine sediment

INTRODUCTION

Every day, chemical and biological measurements are performed by a large number of analysts in laboratories throughout the world and they have to show that the method used is error free and the results obtained are reliable for each parameter analyzed. They need to undertake method validation procedure, a process that has to be re-checked periodically when changing working. During method validation, there are different quality parameters, which characterize the method and must be established such as accuracy; precision; quantification and detection limits; linearity range; sensitivity; and, robustness. Furthermore, laboratories have to design strategies for assuring not only internal quality control (QC), but also some kind of external QC, such as participation in interlaboratory studies and proficiency-testing (PT) schemes [1]. In all these steps particularly in analytical chemistry, reference materials (RMs) provide a readable support in demonstrating the quality of the results as their property values are sufficiently homogeneous and well established.

In a special publication by National Institute of Standards and Technology (NIST), a reference material (RM) is defined as material or substance one or more of whose property values are sufficiently homogeneous and well established to be used for the calibration of an apparatus, the assessment of a measurement method, or for assigning values to materials. A Certified Reference Material (CRM) is a reference material, accompanied by a certificate, one or more of whose property values are certified by a procedure which establishes traceability to an accurate realization of the unit in which the property values are expressed, and for which each certified value is accompanied by an uncertainty at a stated level of confidence. A CRM issued by NIST that also meets additional NIST-specified certification criteria is known as Standard Reference Material (SRM) [2].

All RMs outside the CRM category (i.e. non-certified RMs but with sufficiently homogeneous and well-established property values) have different names in the literature: laboratory RMs, in-house RMs, laboratory control materials or quality-control materials [3]. Sometimes, CRMs are not available for all matrix or analyte combinations and this limitation can be overcome by in-house RMs. A considerable amount of RM is needed to be used on a day-to-day basis. In Neutron Activation Analysis (NAA), CRM has been used routinely as analytical quality control material in order to ascertain the reliability of the result. Therefore, by using in-house RMs, they can provide a relatively cheap option as compared to CRMs.

It is vitally important that in-house RMs are appropriately prepared to ensure that they are fit for intended use and sufficiently stable. An in-house RM shall be homogeneous where the difference between representative sample measurements must be smaller than the overall uncertainty limits of the measurements. The homogeneity of the RM can be conveniently tested using instrumental NAA (INAA). For inorganic constituents analysis, INAA provides a relatively simple with less tedious sample preparation, sensitive, precise, multielement capabilities and non-destructive analytical technique and is remarkably free from analytical interferences with matrix effects being small [4,5].

Since 15 years ago, Neutron Activation Analysis Laboratory of Nuclear Malaysia has involved in marine pollution study extensively through IAEA Regional Cooperation and Forum for Nuclear Cooperation in Asia (FNCA) program. The knowledge of distribution of heavy metal and trace elements provides useful information on the geochemistry of their origin and in the study of oceanographic processes. Reliable and accurate data in such studies can be achieved with matrix RMs assisted. Production of marine sediment in-house material has therefore been proposed as it provides similar matrix properties and offers a low-cost alternative to CRMs.

METHODOLOGY

Sample preparation

A local marine sediment sample coded as ST13 is selected for this study due to its availability in a large amount and its constitution of significant range of elements. The material was dried, ground and sieved. Then it was placed in a polyethylene bottle and homogenized by a rotary device for about a month. The sample was handled with great care to avoid moisture absorption and contamination. Samples were weighed 0.1 to 0.2 g into polyethylene vials and heat-sealed prior to irradiate along with standard, blank and suitable matrix-based reference materials IAEA- Soil 7 and IAEA- SL1 (Lake Sediment) as control materials. Multiple batches of these samples were then packed and sealed in polyethylene rabbits for optimized irradiation.

Sample irradiation and counting

The irradiations were performed in the TRIGA Mark II reactor at Malaysian Nuclear Agency with a thermal neutron flux of $3 \times 10^{12} \text{ n cm}^{-2} \text{ s}^{-1}$. All test samples, standard, CRM and blank were irradiated using 2 types of protocol particularly for short and long lived radionuclide. A high resolution coaxial CANBERRA hyper-pure germanium detector (HPGe) with a resolution of 1.9 keV at 1332 keV gamma-rays line of Co-60 was used for counting the active samples. The spectral data were processed using the spectrum analysis software namely

GINIE 2000. Computations of elemental concentrations were based on relative method and data were reported in dry weight (d.w.).

RESULTS AND DISCUSSIONS

Almost 31 elements have been determined in CRMs and ST13 using INAA. The elemental interferences for most of the elements were eliminated by variation in irradiation, cooling and counting times as given in Table 1. For ST13, number of trial sample is indicate in (x) beside the irradiation protocol.

Table 1: Optimum activation scheme for INAA at TRIGA Mark II Nuclear Malaysia

Irradiation protocol	Irradiation time/cooling time/counting time	Isotope quantified
Short 1 (24)	1min/20min/5min	^{28}Al , ^{49}Ca , ^{52}V , ^{51}Ti
Short 2 (24)	1min/24hr/10min	^{72}Ga , ^{42}K , ^{56}Mn , ^{24}Na
Intermediate (20)	6hr/3days/1hr	^{75}As , ^{82}Br , ^{140}La , ^{122}Sb , ^{153}Sm , ^{239}U
Long (19)	6hr/3weeks/1hr	^{131}Ba , ^{141}Ce , ^{60}Co , ^{51}Cr , ^{134}Cs , ^{152}Eu , ^{59}Fe , ^{181}Hf , ^{177}Lu , ^{145}Nd , ^{86}Rb , ^{46}Sc , ^{177}Ta , ^{160}Tb , ^{233}Th , ^{169}Yb , ^{65}Zn

Data quality

The accuracy and precision of the analytical technique were evaluated by analyzing the CRM using a Z-score calculation [6]. The Z-score of an element concentration is computed based on the following equation:

$$Z - score = \frac{x - c}{\sqrt{u_x^2 + u_c^2}}$$

where x is the analytical results; c is the certified value, u_x is the uncertainty of analytical results, and u_c is the uncertainty of certified value.

The uncertainty of the analytical results were obtained after estimating the contribution from the sources in example errors in weighing, spectral peak counts, background counts and uncertainties in standard value whilst the uncertainty of the certified value was based on the certificate. For acceptance of results: $-2 < z < 2$ is anticipated. However, if $z < -3$ or $z > 3$, it is consider that the result is “out-of-control” and corrective action will be taken.

Data evaluation of two CRM, IAEA- Soil 7 and IAEA- SL1 (Lake Sediment) are presented in Table 2 and 3, respectively. Data obtained indicate good precision and good agreement with the certified values. The relative standard deviations (RSD) of the IAEA Soil 7 results were lower than 20% and relative errors varied from 0 to 14.5%. For IAEA-SL1, the relative error for Eu is 20% whereas the RSD for Tb is slightly above 20%. The concentrations for both elements are given as information values in the certificate for this CRM which implies a lower confidence in their reliability. However, the Z-score values obtained for most of the elements analyzed from both CRMs were $|Z\text{-score}| \leq 2$, indicating that the results are satisfactory and are within the ranges of certified data at the 95% confidence level.

Table 2: Comparison of IAEA-Soil 7 recommended/ information value

IAEA Soil 7					
Element	Analytical value (mg/kg)	Recommended/ information value (mg/kg)	Error %	RSD %	Z-score
Al	47700 ± 1800	47000 ± 3500	1.5	3.8	0.18
As	13.1 ± 1.5	13.4 ± 0.9	2.0	11.6	0.16
Ba	163 ± 25	159 ± 33	2.5	15.3	0.10
Br	6.91 ± 0.57	7 ± 3.5	1.3	8.3	0.02
Ca	168000 ± 9800	163000 ± 8500	3.1	5.8	0.41
Ce	62 ± 5	61 ± 7	1.6	8.1	0.12
Co	9.14 ± 0.39	8.9 ± 0.85	2.7	4.3	0.26
Cs	5.77 ± 0.36	5.4 ± 0.75	6.9	6.2	0.45
Cr	68.7 ± 6.2	60 ± 13	14.5	9.0	0.62
Eu	1.1 ± 0.1	1 ± 0.2	10.0	9.1	0.17
Fe	28000 ± 1300	25700 ± 500	8.9	4.6	1.77
Ga	10.2 ± 2.1	10 ± 2	1.9	20.2	0.06
Hf	5.06 ± 0.54	5.1 ± 0.35	0.9	10.7	0.07
K	12300 ± 670	12100 ± 700	1.7	5.4	0.15
La	28.6 ± 1.3	28 ± 1	2.2	4.6	0.38
Lu	0.31 ± 0.05	0.3 ± 0.15	2.4	16.3	0.05
Mn	642 ± 39	631 ± 23	1.7	6.0	0.24
Na	2400 ± 91	2400 ± 100	0.0	3.8	0.13
Nd	30.7 ± 3.4	30 ± 6	2.5	11.1	0.11
Rb	52.0 ± 3.1	51 ± 4.5	2.0	6.0	0.18
Sb	1.86 ± 0.16	1.7 ± 0.2	9.2	8.8	0.61
Sc	8.88 ± 0.69	8.3 ± 1.02	7.0	7.8	0.47
Sm	5.00 ± 0.06	5.1 ± 0.35	1.9	1.2	0.27
Ta	0.91 ± 0.12	0.8 ± 0.2	13.3	13.2	0.46
Tb	0.65 ± 0.10	0.6 ± 0.2	8.5	15.5	0.23
Th	8.51 ± 0.56	8.2 ± 1.1	3.8	6.6	0.25
Ti	3300 ± 360	3000 ± 550	10.0	10.9	0.42
U	2.75 ± 0.32	2.6 ± 0.6	5.6	11.6	0.21
V	65.6 ± 10.3	66 ± 66	0.5	15.7	0.01
Yb	2.46 ± 0.22	2.4 ± 0.35	2.4	8.8	0.14
Zn	109 ± 8	104 ± 6	5.0	7.5	0.51

Elemental composition of in-house reference material

The concentration for each element was determined as a mean of at least 20 trial samples obtained from several irradiations. Through the optimized methodology 6 major elements (Al, Ca, Fe, K, Na, Ti), 4 minor elements (Ba, Br, Mn, Zn) and 21 trace elements (As, Ce, Co, Cs, Cr, Eu, Ga, Hf, La, Lu, Nd, Rb, Sb, Sc, Sm, Ta, Tb, Th, U, V, Yb) were characterized in candidate sediment for in-house reference material. Mean concentration value, standard deviation, confidence interval at 95%, repeatability and percentage of data accepted from the total trial sample for 31 quantified elements are presented in Table 4.

Table 3: Comparison of IAEA-SL1 (Lake Sediment) recommended/ information value

IAEA SL1 (Lake Sediment)					
Element	Analytical value (mg/kg)	Recommended/ information value (mg/kg)	Error %	RSD %	Z-score
As	27.0 ± 1.1	27.6 ± 2.9	2.3	4.1	0.20
Ba	589 ± 72	639 ± 53	7.8	12.2	0.56
Ce	110 ± 20	117 ± 17	6.0	18.2	0.27
Co	20.6 ± 1.0	19.8 ± 1.5	4.0	5.0	0.44
Cs	7.13 ± 0.44	7 ± 0.9	1.8	6.2	0.13
Cr	104 ± 8	104 ± 9	0.4	7.6	0.04
Eu	1.92 ± 0.18	1.6 ± 0.5	20.0	9.6	0.60
Fe	73800 ± 3600	67400 ± 1700	9.5	4.9	1.62
Ga	22.9 ± 2.7	23.7 ± 5.1	3.2	11.7	0.13
Hf	4.61 ± 0.37	4.2 ± 0.6	9.6	8.1	0.57
K	14200 ± 1100	14500 ± 2100	2.1	7.7	0.15
La	49.8 ± 4.2	52.6 ± 3.1	5.3	8.5	0.53
Lu	0.53 ± 0.07	0.54 ± 0.13	2.1	15.1	0.08
Mn	3370 ± 230	3460 ± 160	2.6	6.8	0.32
Na	1800 ± 100	1700 ± 100	5.9	5.6	0.47
Rb	114 ± 9	113 ± 11	1.3	7.8	0.10
Sb	1.47 ± 0.20	1.31 ± 0.12	12.1	13.7	0.68
Sc	17.7 ± 1.1	17.3 ± 1.1	2.0	6.1	0.23
Sm	8.58 ± 0.34	9.25 ± 0.51	7.3	4.0	1.09
Ta	1.34 ± 0.17	1.58 ± 0.58	15.4	12.9	0.40
Tb	1.18 ± 0.30	1.4 ± 0.46	15.4	25.6	0.39
Th	14.4 ± 0.5	14 ± 1	2.8	3.4	0.35
U	3.94 ± 0.21	4.02 ± 0.33	2.1	5.4	0.21
V	172 ± 22	170 ± 15	1.2	12.5	0.08
Yb	3.71 ± 0.46	3.42 ± 0.65	8.6	12.4	0.37
Zn	239 ± 27	223 ± 10	7.0	11.1	0.55

The repeatability results for most elements were below 17%. However, only Ga showed slightly high deviation among the samples. The results demonstrated the percentage of data accepted for the calculations of mean value were above 70% except for As, Nd and Ti. Rejected data or outlier which distant from the range of confidence interval was removed from the data set may due to statistical counting error, error during measurement, variation in neutron spectrum during irradiation or material inhomogeneity.

Table 4: Recommended values of elements of proposed in-house reference material ST13

Element	Mean (mg/kg)	SD (mg/kg)	95% Confidence Interval (mg/kg)	Repeatability %	Data accepted %
Al	67700	2280	62300-68000	3.4	71
As	7.68	0.39	6.90-8.46	5.1	65
Ba	158	14	130-185	8.9	74
Br	101	9	834-184	8.9	95
Ca	22100	1800	18200-26400	8.1	75
Ce	86	9	68-104	10.5	95
Co	5.94	0.65	4.64-7.24	10.9	95
Cs	9.61	0.76	8.09-11.13	7.9	95
Cr	50.8	6.9	37.1-64.6	13.5	95
Eu	0.86	0.06	0.74-0.98	7.1	84
Fe	22900	2150	18600-27300	9.4	95
Ga	15.8	3.9	8.1-23.6	24.6	71
Hf	10.42	1.09	8.24-12.6	10.5	95
K	15000	780	13400-16500	5.2	88
La	40.50	2.30	35.9-45.0	5.7	90
Lu	0.47	0.06	0.35-0.59	13.4	84
Mn	366	25	315.0-417	7.0	88
Na	22300	740	20800-23800	3.3	92
Nd	31.1	3.0	25.1-37.1	9.6	68
Rb	101	6	90-113	5.9	95
Sb	0.60	0.09	0.42-0.78	15.3	70
Sc	8.62	0.84	6.94-10.3	9.7	95
Sm	6.37	0.40	5.57-7.17	6.3	75
Ta	2.48	0.33	1.82-3.14	13.2	84
Tb	0.79	0.10	0.59-0.99	12.3	89
Th	24.4	2.2	20.0-28.8	9.0	95
Ti	3300	380	2560-4070	11.5	63
U	5.10	0.52	4.06-6.14	10.2	70
V	62.7	7.6	47.6-77.9	12.1	88
Yb	3.08	0.51	2.06-4.10	16.6	79
Zn	75.7	6.2	63.3-88.2	8.2	79

CONCLUSIONS

The sample of ST13 can be applied as laboratory quality control material for routine analysis particularly in NAA. This may help in reducing the usage of CRM as well as decreasing the cost of sample analysis. It also can be used in the development and validation of laboratory methods and is useful for evaluating the proficiency of the chemists and laboratories. Furthermore, the nondestructive, multielement and highly sensitive capability of INAA can be confidently used to characterize the sediment material with relatively high precision. The development of the studied sediment material will definitely provide a useful addition to the inventory of reference material that can be used for marine pollution studies.

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