

## Intercomparison Exercises; A Requirement for Accurate and Precise Analytical Data

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**Summary:** External evaluation of laboratory results and procedures can be carried out by participation in intercomparison exercises. The results of the International Atomic Energy Agency - Marine Environmental Laboratory (IAEA-MEL), Monaco intercomparison exercise IAEA-158, marine sediment are presented and discussed in this paper. Using four different irradiation protocols instrumental neutron activation analysis (INAA) was used to quantify 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 reference material (RM). IAEA-405 (Estuarine Sediment) and IAEA-SL1 (Lake Sediment) were used as compatible matrix RMs for quality assurance (QA) purposes. The Z-scores showed our results to be in very good agreement with the IAEA certified values. Furthermore the IAEA placed our laboratory in Group 1 for having  $\geq 90\%$  of the data with acceptable Z-scores.

### Introduction

There are numerous factors and protocols which can be used to validate data and ensure reliable analytical results. A good quality assurance and quality control (QA/QC) programme includes both internal performance checks for day to day validation and regular external performance evaluations for an independent assessment of analytical proficiency. Concurrent analysis of a material of known composition that is of similar matrix to the sample, *i.e.* a reference material (RM), can confirm the accuracy of the analytical process and provide internal performance check. Furthermore in the long run such data can be used to evaluate laboratory performance. An intercomparison exercise (ICE) or a proficiency test (PT) provides independent external laboratory assessment. Such inter-laboratory comparisons (ILCs) are essential for checking the accuracy of a laboratory's analytical results and to develop better analytical procedures.

RMs play a vital 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 [1-3]. The International Organization for Standardization (ISO) Guides 32: 1997 (E) [4] and 33: 2000 (E) [5] list comprehensive uses of RMs 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. [6, 7] 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 [8]. For this reason a diverse inventory of well-characterized RMs for trace elements determination is required apart from primary RMs, which are synthetically prepared. This is because 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 [7]. A regular independent assessment of the technical performance of a laboratory is therefore 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 [9, 10]. For this reason regular participation in PTs and ILC exercises is required.

To maintain confidence in our analytical capabilities, the neutron activation analysis laboratory (NAA) at the Miniature Neutron Source Reactor (MNSR), Chemistry Division, Directorate of Science, Pakistan Institute of Nuclear Science and Technology (PINSTECH) has regularly participated in PTs and ILCs conducted by the International Atomic Energy Agency (IAEA), World Health Organization/Global Environmental Monitoring System/IAEA (WHO/GEMS/IAEA), the Chinese Academy of Sciences (CAGS) as well as by Environmental Monitoring Laboratory (EML), US Department of Energy (DOE) for the past 30 years [11-19].

The NAA/MNSR laboratory was certified as a testing laboratory by the Pakistan National

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Accreditation Council (PNAC) on the 19<sup>th</sup> of April 2005 [20]. It was re-assessed and its certification was continued for further 3 years in 2008. Prerequisites of certification include annual audits conducted by the PNAC as well as maintenance of the laboratory quality system documents and records. According to ISO standards, section 4.10 continual improvements in the management system of a testing laboratory are also mandatory [21]. Therefore the results obtained from participation in PTs and intercomparison exercises are studied from time to time to determine whether experimental procedures need to be changed or improved.

The long range transport and enrichment of pollutants in sediments from estuaries is of major concern due to local anthropogenic emissions from nearby urban and industrial areas [22, 23]. The knowledge of composition and distribution of trace elements provides useful information on the geochemistry of their origin and in the study of oceanographic processes [24]. Reliable and accurate data in such studies requires matrix RMs. To address this problem IAEA-MEL launched a worldwide intercomparison exercise for the determination of trace elements in IAEA 158 marine sediment sample in 2006. The NAA/MNSR laboratory took part in this exercise. The results obtained for the World-Wide Intercomparison Exercise on "The determination of trace elements in IAEA-158 Marine Sediment" were compiled and have been published in a report by the IAEA. [25]. The results obtained have been compared with the IAEA results. Any shortcomings and differences are discussed in this paper.

#### *Uncertainty Evaluation*

At the NAA/ MNSR laboratory uncertainty analysis is carried out using the methodology outlined in JCGM 100: 2008 [26]. In this work instrumental neutron activation analysis (INAA) was used for obtaining quantitative data. For this technique we identify the type A (random variation in measurements, counting errors, weighing errors, spectral interferences, summing peaks corrections, uncertainty due to matrix effect) and type B sources of uncertainties (uncertainty associated with the calibration of the balance and the HPGe detector and uncertainties quoted in the RM certificate) and combine them in the following way:

$$Unc_{Combined} = 2 * \sqrt{\sigma^2 + Unc_C^2 + Unc_W^2 + Unc_B^2 + Unc_D^2 + Unc_{RM}^2} \quad (1)$$

where  $\sigma$ ,  $Unc_C$ ,  $Unc_W$ ,  $Unc_B$ ,  $Unc_D$  and  $Unc_{RM}$  are the standard deviation of the mean obtained from up to 6

values (samples are in triplicate and 2 RMs are used), counting, weighing, balance calibration, HPGe detector calibration and RMs uncertainties respectively. The coverage factor 2 implies a confidence level of 95.45%. The first 3 terms are the type A and the last 3 are the type B sources of uncertainty. In this intercomparison exercise only the standard deviation and the limits of detection (LODs) were required by the IAEA along with the mean concentration data. However uncertainties were also obtained using a coverage factor of 1 (68.27% confidence interval).

From equation 1, it can be seen that the measurement uncertainty can be reduced by reducing all its sources. However limitations are imposed on analytical results by the instruments used and their capabilities as well as the standards and reagents used in carrying out a measurement. Using optimized analytical protocols the sources of uncertainties listed above are minimized. However in our analysis mostly IAEA RMs are used for quantification and for quality assurance and method validation purposes. These generally have higher cited uncertainties than National Institute of Standards and Technology (NIST) standards. Moreover the RM producers provide certified as well as information values for some elements on the RM certificates. In order to obtain an estimate of the uncertainty for an element for which only an information value is given, adopting a worse case scenario approach, the given value is divided by SQRT(3) assuming a rectangular distribution. However from past experience it can be concluded that the given information value most probably lies near the centre as compared to the edges the information value should be divided by SQRT(6), assuming a triangular distribution to obtain a measure of the uncertainty. The latter has been adopted here as the RMs used in this study are commonly used in analysis and in the past the information values have provided accurate and precise results. As mentioned earlier Limits of detection (LODs) were calculated using three standard deviations as recommended by Committee of Environmental Improvement of the American Chemical Society [27-28].

#### *Laboratory Performance Evaluation Criteria*

For any intercomparison exercise the IAEA determines consensus/ assigned values for major, minor and trace elements using the data submitted by all the participants of the exercise. Using these, the IAEA evaluates the data submitted by various laboratories by calculating the following parameters [29].

Relative Bias

The relative bias is calculated using the equation:

$$R.Bias = \frac{(Value_{Analyst} - Value_{IAEA})}{Value_{IAEA}} * 100\% \quad (2)$$

R. Bias is generally < 20-25% for results which are close to the consensus or assigned results.

Z-score

The Z-scores are obtained for each analyte using the formula:

$$z - score = \frac{(Value_{Analyst} - Value_{IAEA})}{\sigma} \quad (3)$$

where  $\sigma = 12.5\%$  of the consensus/ assigned value.

If  $|Z| \leq 2$  satisfactory performance  
 $2 < |Z| < 3$  questionable performance  
 and  $|Z| \geq 3$  unsatisfactory performance

Laboratory Classification

Finally the laboratories are categorized according to the criteria given below:

Group 1 laboratories scoring  $|Z| < 3$  for  $\geq 90\%$  of the data;

Group 2 laboratories scoring  $|Z| < 3$  for 75% to < 90% of the data;

Group 3 laboratories scoring  $|Z| < 3$  for 50% to < 75% of the data;

Group 4 laboratories scoring  $|Z| < 3$  for < 50% of the data

Results and Discussion

In this work twenty seven trace elements were quantified in IAEA-158 (sediment) using INAA. The concentrations of all the elements reported to IAEA were corrected for the moisture content of 6.79%. By variation in irradiation, cooling and counting times, as given in Table-1 the elemental interferences for most of the elements were eliminated. Nuclear interferences were found to be negligible as fast flux in the MNSR type reactor is very low. The interference of  $^{28}\text{Mg}$  with  $^{56}\text{Mn}$  was dealt with by measuring Mn in the second counting scheme (2m/2h/5min) where the peak of  $^{56}\text{Mn}$  was resolved from the  $^{28}\text{Mg}$  peak at 843 keV. Spectral interferences for the determination of  $^{203}\text{Hg}$  in the

presence of  $^{75}\text{Se}$  and  $^{65}\text{Zn}$  in the presence of  $^{46}\text{Sc}$  were corrected as mentioned in our earlier works [30, 8].

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	30s/2min/2min	$^{28}\text{Al}, ^{51}\text{V}$
Short	2min/2hr/5min	$^{56}\text{Mn}, ^{155}\text{Sm}$
Intermediate	1hr/2days/30min	$^{76}\text{As}, ^{82}\text{Br}, ^{140}\text{La}, ^{42}\text{K}, ^{24}\text{Na}$
Long	5hrs/2 weeks/2hr	$^{141}\text{Ce}, ^{60}\text{Co}, ^{51}\text{Cr}, ^{134}\text{Cs}, ^{152}\text{Eu}, ^{59}\text{Fe}, ^{181}\text{Hf}, ^{177}\text{Lu}, ^{145}\text{Nd}, ^{86}\text{Rb}, ^{124}\text{Sb}, ^{46}\text{Sc}, ^{75}\text{Se}, ^{153}\text{Sm}, ^{177}\text{Ta}, ^{178}\text{Tb}, ^{233}\text{Th}, ^{175}\text{Yb}, ^{65}\text{Zn}$

A requirement of a PT or intercomparison is that analysis is carried out as it would be for a routine sample. Therefore the data presented in this work were obtained using replicate samples using multiple irradiation schemes as outlined in our laboratory scope. The irradiation schemes used and the methodology adopted have been devised to account for and deal with all possible spectral interferences [13, 8]. Furthermore, the standards used for quantification; IAEA SL1 (lake sediment) and IAEA-405 (estuarine sediment) are soil based therefore should have a similar matrix to the test sample. High-biased results can originate from contamination during either sample preparation (e.g. digestion step) or analysis. Therefore great care has to be taken to check analytical procedures (e.g. quality of purified water and reagents) and try to improve the cleanliness of the working environment. For example, dust is the most common atmospheric source of contaminants for trace elements in laboratories. As INAA does not involve any sample preparation steps such as digestion the results obtained should be accurate and not suffer from this issue. However it is ensured that clean working conditions are maintained.

The QA data for these standards are given in Table-2. From these results it can be seen that up to 30 elements can be quantified with confidence using these two RMs. The QA data for the two certified RM, IAEA-SL1 and IAEA-405 are also presented in Fig. 1 and 2. From these plots it can be seen that our results match well with the certified data for both of the RMs analyzed as all data points lie on the (IAEA Values) =  $m \cdot (\text{Our Values}) + c$  line where  $m \cong 1.0$  and  $c = 0.0$  and the chi-squared for both plots is also  $\cong 1.0$ . Table-2 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 of these three

elements are given as information values in the certificate for this RM which implies a lower confidence in their reliability. The matrix of the proposed RM is quite similar to IAEA-405 and it can be seen from Table-2 that all the trace elements were determined with % deviation of <5% between the IAEA and our results. From this table and plots it can be seen that the measured concentrations and reference values show no significant difference. This therefore provides us confidence that the results of this intercomparison will be accurate as observed in previous exercises [13, 17-19].

Table-2: Comparison of IAEA results with results obtained in current study. All concentrations in mg/kg).

Element	IAEA SL1		IAEA 405	
	Our Value	IAEA Value	Our Value	IAEA Value
Al	89310±5790	(89000)	76460±5490	77900±5200
As	27.2±2.2	27.5±0.30	23.46±1.17	23.6±0.70
Ba	641.7±42.3	639±5.11		
Br	5.70±2.50	6.82±1.73	102.1±20.2	85.0±25.0
Ce	116.7±6.0	117.0±1.8		
Co	19.6±1.9	19.8±0.2	13.4±1.3	13.7±0.7
Cr	103.7±3.5	104.0±0.9	83.0±4.6	84.0±4.0
Cs	7.0±0.3	7.0±0.1	12.7±0.7	12.5±2.1
Eu	1.54±0.10	1.60±0.50	1.20±0.10	1.25±0.36
Fe	67230±1910	67400±200	37600±1050	37400±700
Hf	4.09±0.21	4.16±0.06	5.70±0.30	5.80±0.87
Hg	0.14±0.21	0.13±0.05	0.84±0.12	0.81±0.04
K	15100±560	15000±2100	25030±1630	24900±7200
La	53.8±5.1	52.6±0.3	41.0±4.0	40.4±7.3
Lu	0.51±0.04	0.54±0.13	0.47±0.05	0.47±0.19
Mn	3440±70	3460±17	497±15	495±11
Na	1745±78	1720±12	15190±5000	
Nd	43.4±3.2	43.8±0.3		
Rb	112.0±9.2	113.0±1.1		
Sb	1.28±0.13	1.31±0.01	1.87±0.19	1.81±0.19
Sc	17.3±0.9	17.3±0.1	13.5±0.8	13.5±2.0
Se	2.75±0.34	2.85±1.53	0.45±0.06	0.44±0.12
Sm	9.15±0.66	9.25±0.06	6.99±0.38	6.86±0.36
Sn	3.6±2.0	(4.0)	8.5±4.0	7.6±1.3
Ta	1.65±0.10	1.58±0.46		
Tb	1.35±0.13	1.40±0.58	0.96±0.06	0.93±0.43
Th	14.20±0.98	14.00±0.10	14.36±0.55	14.30±2.10
V	171.7±17.2	170.0±1.5	97.7±15.0	95.0±5.0
Yb	3.51±0.28	3.42±0.06	2.99±0.32	3.04±7.00
Zn	271±50	223±10	275±11	279±7

( ) Given as information values by the IAEA

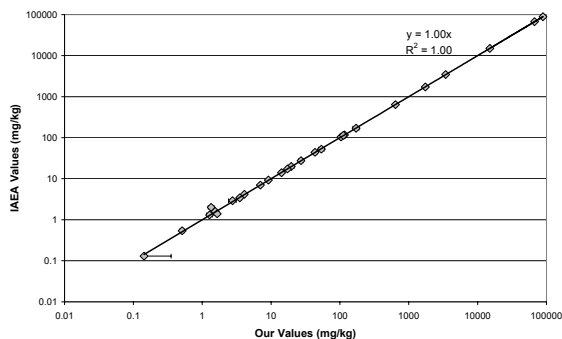


Fig. 1: QA plot for IAEA-SL1 (Lake Sediment).

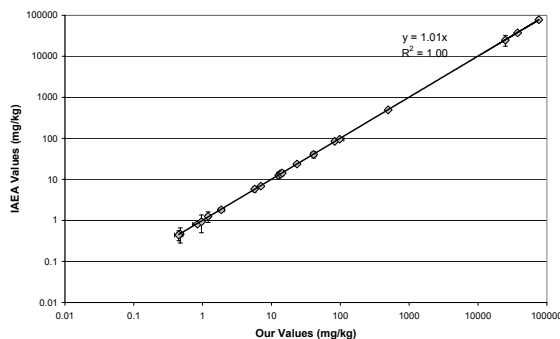


Fig. 2: QA plot for IAEA-405 (Estuarine Sediment).

Elemental concentrations in IAEA-158 determined using INAA are summarized in Table-3. These values have been published in our earlier work [31]. However as the IAEA has recently published a report on this intercomparison exercise the results have been compared with the IAEA data in this table [25]. 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 proposed sediment RM. Mean concentration value, uncertainty, detection limit and repeatability for 27 quantified elements are presented in this table. The LODs and uncertainties were obtained as discussed in section 1. The Z-scores and R.Bias were calculated for each analyte and are also presented in Table-3. Close examination of Table 3 shows that our values are in close agreement with the IAEA values. These include the data for elements which the IAEA has not certified but has given as information values (Br, Hf, Lu, Sc, Ta, Tb, Th and Tb). Data for Nd and Se have also been included in this table. Insufficient data was submitted for these elements to the IAEA. Although the data submitted by intercomparison participants for these two analytes are quite variable our values do lie in the concentration range given. Our data has relatively larger values of uncertainty which implies that all possible uncertainty sources (worst case scenario) have been identified and used including the bias of RM material. The uncertainties cited in the certificates for these RMs can be high; *i.e.* 36.7% for Ta in IAEA-SL1. Furthermore this can be problematic when only information values are given. In such cases determining the uncertainty for elements with information values may be ambiguous and variable from laboratory to laboratory.

Table-3: Analysis of IAEA-158 intercomparison results to determine laboratory performance. All concentrations in mg/kg.

Element	This Study				IAEA Values		Rel Bias	z-score	Score	
	Mean	Unc	RSD %	SD	LOD	Mean				SD
Al	44300	4440	7.4	3270	1220	51800	6475	-14.41	-1.15	A
As	8.24	1.26	10.7	0.88	0.25	11.50	1.44	-28.39	-2.27	A
#Br	216	66	9	19	114	224	28	-3.67	-0.29	A
Ce	63.02	15.96	6.0	3.81	1.30	61.10	7.64	3.14	0.25	A
Co	8.87	2.14	6.7	0.59	0.30	9.20	1.15	-3.55	-0.28	A
Cr	74.0	16.1	5.3	3.9	3.3	74.4	9.3	-0.53	-0.04	A
Cs	3.65	0.54	4.9	0.18	0.45	3.73	0.47	-2.25	-0.18	A
Eu	0.97	0.30	9.3	0.09	0.06	1.08	0.13	-10.17	-0.81	A
Fe	26080	1390	4.2	1100	360	26300	3290	-0.83	-0.07	A
#Hf	5.7	0.9	3.5	0.2	0.2	6.2	0.8	-7.76	-0.62	A
K	19060	5990	11.5	2200	3450	20000	2500	-4.71	-0.38	A
La	28.6	5.8	8.7	2.5	2.0	30.2	3.8	-5.45	-0.44	A
#Lu	0.28	0.11	10.7	0.03	0.02	0.31	0.04	-9.58	-0.77	A
Mn	332	46	12.9	43	2	356	45	-6.87	-0.55	A
Na	23760	1890	3.7	890	190	23800	2980	-0.18	-0.01	A
*Nd	31.0	6.9	9.7	3.0	2.2	21-37	1.3-23.8%			
Rb	73.6	10.4	9.5	7.0	24.4	82.0	10.25	-10.21	-0.82	A
Sb	1.34	0.21	10.4	0.14	0.30	1.34	0.17	-0.06	0.00	A
#Sc	8.1	1.2	3.7	0.3	0.1	8.3	1.0	-2.20	-0.18	A
*Se	0.46	0.14	10.9	0.05	0.19	0.22-16	3.9-41.4%			
Sm	4.6	0.4	6.5	0.3	0.1	4.9	0.6	-6.54	-0.52	A
#Ta	0.93	0.26	10.8	0.10	0.05	0.97	0.12	-3.96	-0.32	A
#Tb	0.70	0.33	5.7	0.04	0.03	0.63	0.08	10.71	0.86	A
#Th	8.3	1.3	4.8	0.4	0.2	8.9	1.1	-6.63	-0.53	A
V	63.92	10.43	6.6	4.20	16.82	73.00	9.13	-12.44	-1.00	A
#Yb	1.94	0.57	9.3	0.18	0.25	2.08	0.26	-6.57	-0.53	A
Zn	151.6	17.0	9.0	13.5	3.6	140.6	17.6	7.13	0.57	A

# Given as information values by the IAEA

\* Not included in the final certificate by the IAEA

The data in Table-3 was further scrutinized and shows that all of the reported data has R. Bias <20% and Z-scores less than 2 apart from As. The R. Bias for this analyte is >28% and its Z-score is >2 but <3 making its value questionable. The lower As value may originate from an over correction due to the presence of bromine in the sample, which may give rise to spectral problems due to inadequate resolution of the two peaks or limitations with the evaluation software. Br is found in higher amounts in sediment and in this sample its concentration is an order of magnitude higher than that of As. Table-3 also shows that all reported results have acceptable Z-scores. Therefore for this intercomparison exercise our laboratory is placed in Group 1 ( $|Z| < 3$  for  $\geq 90\%$  of the data). This shows that the procedures employed in our laboratory are good and produce accurate and precise results.

In our earlier publication the results for Al, Ca, Fe, K, Mn, Na and Ti were presented as common oxides which occur in sediments; *i.e.* Al<sub>2</sub>O<sub>3</sub>, CaO, Fe<sub>2</sub>O<sub>3</sub>, K<sub>2</sub>O, MnO, Na<sub>2</sub>O and TiO<sub>2</sub> [31]. The oxides CaO, MgO and TiO<sub>2</sub> were not detected in IAEA-158 whereas SiO<sub>2</sub> was not determined using INAA but is a major component of sediments. The above oxides amount to  $\cong 17.64\%$  of the total mass. The remaining elements occur in trace amounts so around 80% of the sediment is probably SiO<sub>2</sub>. The results obtained fall well within the ranges of trace elements cited for commonly available sediment certified reference materials (CRMs); *i.e.* 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 RMs for use in environmental, marine and geological studies. Furthermore a large number of elements (27) including the REEs Ce, Eu, La, Lu, Nd, Sm, Tb and Yb have been quantified in this sample.

IAEA-158 marine sediment sample was analyzed using INAA as part of the IAEA-MEL intercomparison exercise. Twenty seven elements were quantified in this sample. The IAEA results were found to be in close agreement with the reported results as all Z-scores were acceptable placing our laboratory in Group 1. Our experience of analyzing such samples, the good performance of our laboratory in the past and current international intercomparison exercises and the QA data obtained during this study have provided us confidence in the reliability of our results. Furthermore the certification of this RM has provided a useful addition to the inventory of RMs that can be used for the pollution migration studies.

## Experimental

### Sample Preparation

In November 2004, a large quantity of marine sediment was collected from Kilbrannan Sound, south east of the island of Arran, in the Clyde River estuary, Scotland, UK. The material was freeze dried and sent to IAEA MEL through collaboration with the QUASIMEME Laboratory Performance Studies Programme. The dried material was hand sieved (315  $\mu\text{m}$ ) by MESL staff. The sieving cut-off value was selected to ensure that physical properties of the material are sufficiently uniform whilst retaining sufficient material to make adequate number of units. The particle size distribution profile of the bottled material was measured using a MALVERN Mastersizer Micro v2.12 instrument; a device which uses the diffraction of laser light to determine the range of particle sizes in the sample. The particle size distribution profile of IAEA-158 shows that approximately 70% of the particles have sizes below 100  $\mu\text{m}$ . It is important that an RM substance is finely divided and physically as "homogeneous" as possible, such that sub-samples are as representative as possible and physical processes such as digestion (and moisture determination) are reproducible.

Aliquots of about 25 g were packed into glass bottles with polyethylene 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) [32]. The prepared samples were distributed to 140 laboratories around the world by IAEA-MEL for an intercomparison exercise. From these 140 laboratories, results from 93 laboratories in 41 countries were received by the end of 2006.

The samples were analyzed as such in our laboratory without any further processing. However each sample was handled with great care to restrict any contamination and moisture absorption. About 200mg of IAEA-158 in triplicate along with suitable matrix-based RMs; 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 a polyethylene rabbits for irradiation.

#### Sample Irradiation and Counting

The sealed targets were loaded and irradiated according to the optimized schemes presented in Table 1 at the Pakistan Research Reactor-II (PARR-II), which is a 27 kW, MNSR reactor with a thermal neutron flux of  $1 \times 10^{12} \text{ cm}^{-2} \text{ s}^{-1}$ . The same irradiation, cooling and counting protocols were adopted for the sample and the control materials. The irradiated samples, after the desired cooling periods, 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 a 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  $^{60}\text{Co}$  and peak to Compton ratio of 40:1. The data files were subjected to calculations on our validated in-house computer programs [33]. All necessary corrections (background subtraction etc) were applied and the final results obtained on dry weight basis. The moisture content was obtained by drying a sub-sample (not taken for analysis) at  $105^\circ\text{C}$  for 24 hours. Error propagation rules were applied at each stage of the calculations as mentioned earlier 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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