

Analytical Data: Reliability and Presentation

Naila Siddique* and Shahida Waheed

*Chemistry Division, Pakistan Institute of Nuclear Science and
Technology, P.O Nilore, Islamabad 45650, Pakistan.
nailasiddique@yahoo.ca**

(Received on 21st March 2013, accepted in revised form 8th August 2013)

Summary: Chemical analysis whether it is used to determine the composition of a sample or to devise a procedure for testing or preparation of another sample requires systematic experiment design and implementation. In order to determine and verify the validity of results various methods are employed to evaluate the data obtained. This process enables the analyst not only to understand the results but to find possible reasons for differences and similarities between samples. A simple scheme for carrying out analysis in order to obtain valid and reliable results is outlined in this paper. Moreover the importance of using reference and quality control materials to obtain quantitative results is also highlighted. To evaluate the performance and capability of a laboratory or an analytical procedure, parameters such as relative bias, z-scores, u-test, tests for accuracy and precision etc can be used. The use and significance of these parameters is explained using examples in this manuscript. Uncertainties and errors in measurement as well as the limits of detection (LOD) of an experimental procedure can also provide vital information about the data obtained. Simple calculations are used to explain how these can be obtained and what their magnitudes imply.

Key words: Quality assurance (QA), Quality control (QC), Reference materials (RMs), Relative bias, Z-score, U-test, Precision, Accuracy, Uncertainty, Limits of detection (LODs).

Introduction

A basic requirement of any scientific study is reliable compositional data. For this purpose various analytical techniques may be used depending upon the nature of the results required. For example if elemental composition is required then techniques such as inductively coupled plasma atomic emission spectrometry (ICP-AES), atomic absorption spectrometry (AAS), neutron activation analysis (NAA), X-ray fluorescence spectroscopy (XRF), proton induced X-ray emission (PIXE) etc can be used. When analyzing organic samples, chromatographic techniques, such as, gas chromatography (GC), high performance liquid chromatography (HPLC), or other spectroscopy techniques such as nuclear magnetic resonance (NMR), infrared spectroscopy (IR), Raman spectroscopy etc can be used. The selection of an analytical technique depends on the type of information required and at what sensitivity level. For trace analysis involving small amounts of samples a sensitive and versatile technique is needed. If the selected technique does not involve laborious, costly and time consuming sample preparation steps prior to measurements then possible contamination or loss of sample is avoided. No one technique is ideal and therefore the best suited available technique is selected for analysis. [1-4]

The neutron activation analysis laboratory (NAA) at the Miniature Neutron Source Reactor (MNSR), Chemistry Division, Pakistan Institute of Nuclear Science and Technology (PINSTECH) was

certified as a testing laboratory by the Pakistan National Accreditation Council (PNAC) on the 19th of April 2005. [5] Since then it has been re-assessed twice and its certification has been extended till 11-04-2016. This certification implies that the data reported by the NAA/ MNSR Laboratory is reliable and acceptable to the PNAC if submitted by any industry or organization. Reports containing compositional data are routinely required for trade and to prove the quality of products.

In scientific literature only data which have been obtained using reliable and tested procedures are considered acceptable. To produce reliable results the analysts must follow systematic procedures. The procedures used should be tested using calibration procedures and the analysis of reference or standard samples. Moreover the analysis should be carried out efficiently so that the expenditure of chemical reagents and time is kept to a minimum. This goal is most easily achieved when fewer and simpler sample preparation steps are employed.

This manuscript was undertaken to present the methodology routinely followed for elemental analysis using NAA at the NAA/MNSR Laboratory. The information provided in this paper which includes step-wise procedure from sample's arrival at the laboratory to the submission of results is provided as a guide for other analytical chemists. The basic aim of this manuscript is to educate, inform or remind analysts of good experimental design,

*To whom all correspondence should be addressed.

sequential and methodical analysis and proper way of reporting the results. Therefore this paper will focus on the data obtained and how to understand and present it to show its validity and reliability. The basic concepts provided here can be applied to the results obtained using any analytical procedure to obtain valid results in as short time as possible. Hence “mock results” have been used in examples to enable the reader to better understand the information provided.

Chemical Analysis

Analytical results obtained are only as reliable as the method and care employed to obtain them. Therefore analytical procedures are carefully developed and tested prior to analysis of a new type of sample. Fig. 1 shows a flow diagram for carrying out chemical analysis. From this figure it can be seen

that once sampling has been completed and a sample provided to the analyst, the analyst has to select a suitable analytical technique and prepare the sample for analysis. In order to do this, steps may be required which involve drying or grinding of the sample to obtain a homogeneous sample which fully represents the test sample. After this, representative sub-samples of the test sample are taken and prepared for measurement. The sample preparation step is technique dependant and may involve the formation of the sample in the form of a pellet or disc for XRF and PIXE analysis or a dissolution /digestion procedure to obtain the sample in a liquid form for GC, HPLC, AAS and ICP-AES. Some non-destructive techniques such as NAA may not even require a sample preparation step which makes contribution from blank minimal. [6].

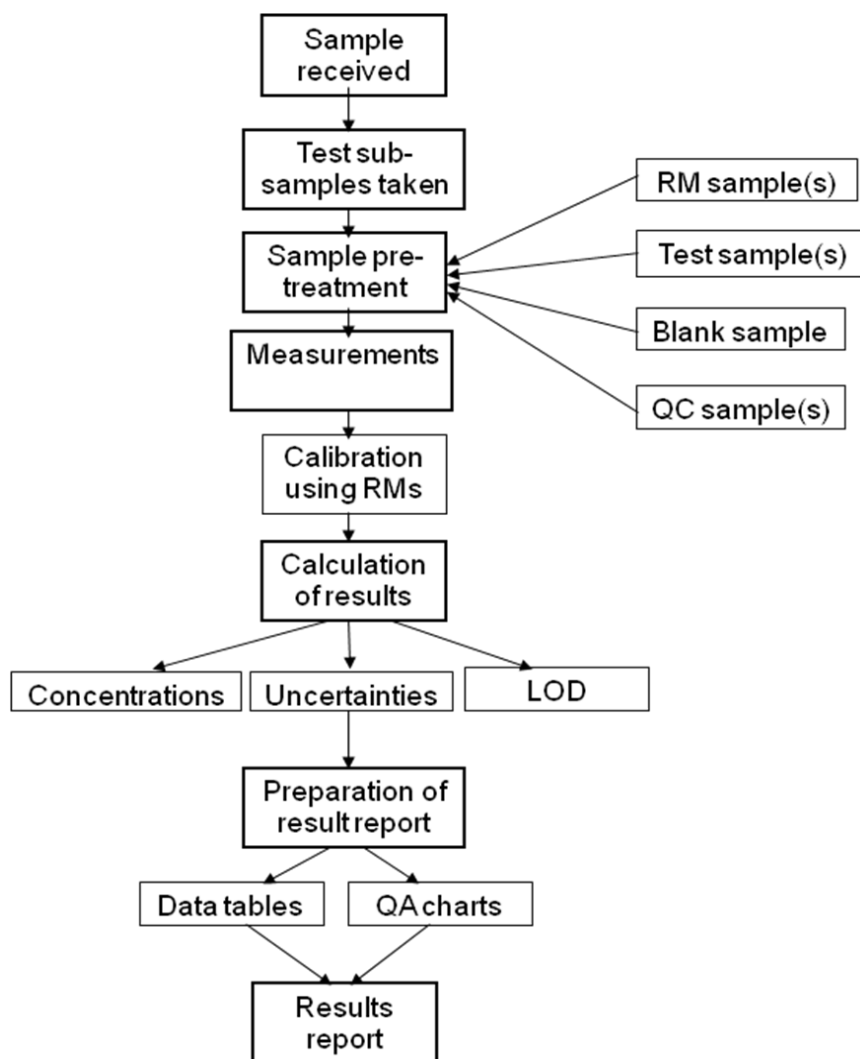


Fig. 1: Schematic diagram to show the steps involved in analytical analysis.

In order to carry out analysis the following samples are prepared:

1. Test sample, usually measured in triplicate or more
2. At least 2 quality control (QC) materials whose composition is known may be obtained from reputable RM producers
3. Reference materials (RMs) which are used for calibration of instrument and to obtain quantitative data. These should consist of ~5 samples of different concentrations of an element/ compound being studied. The data obtained for these RMs are used to prepare calibration plots. Moreover certified RMs along with synthetic or laboratory prepared RMs can also be used to increase the number of elements/ compounds determined in a single analytical procedure.
4. In cases where sample preparation involves solvents or substrates a blank is also prepared.

The QC material, RM material and blank are prepared following the procedure employed for test sample preparation, the only difference being is that in place of the test sample the QC material, RM material and substrate (blank) are used respectively. In the next section the various calculations undertaken to obtain the results of Fe concentration in a test sample are given as an example.

Results and Discussion

The analytical techniques used for analysis will provide results for the RM, QC material, blank sample and test sample. In order to understand the tools used to obtain and evaluate the results obtained and what they signify, the Fe concentration in a test sample is used as an example. An important point to note is that the number of significant figures used to report the data should be realistic and consistent when performing calculations involving multiple steps.

To obtain analytical results the instrument needs to be calibrated as discussed below. However before quantitative data can be presented and explained it is best to first discuss measurement uncertainty and limits of detection (LODs). These are an essential part of any chemical analysis and are required when result reports are prepared.

Uncertainty Measurement

All analytical results are reported along with their uncertainties or errors. These provide an

indication about the spread or variation in the value of the result provided. Measurement uncertainty analysis may be performed using the methodology outlined in JCGM 100: 2008. [7] To calculate the uncertainty for a technique the uncertainty budget has to be prepared and all possible type A and type B sources of uncertainties identified. For NAA, Type A uncertainties or the random errors which occur in any measurement include measurement standard deviation (SD), uncertainty in peak area, weighing errors, errors in volume measurement, spectral interferences, summing peaks corrections, uncertainty due to matrix effect etc while type B sources of uncertainties include uncertainty associated with calibration of instruments such as weight balance and the detector used and uncertainties quoted in the RM certificate. Both these uncertainties can be combined in the following way:

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

where σ , Unc_{PA} , Unc_W , Unc_V , Unc_B , Unc_D , Unc_{RM} etc are the variation in measurement (standard deviation), uncertainty in estimation of peak area, weighing, volume, balance calibration, HPGe detector calibration and RMs uncertainties respectively. The first 4 terms are the type A and the last 3 are the type B sources of uncertainty. The uncertainties listed in the above equation are by no means exhaustive and will differ from technique to technique. Therefore the analyst has to determine all possible sources of uncertainty in their analytical procedure. Coverage factor of $k=1$ to 3 can be used in the above equation. Values of $k=1$, 2 and 3 imply confidence intervals of 68.27%, 95.45% and 99.99% respectively.

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. It is best to use RMs which has low uncertainties for all possible elements/ compounds. This may not be possible as RM producers provide recommended 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 an information value is given, adopting a worse-case scenario approach, the given value is divided by $\sqrt{3}$ assuming a rectangular distribution. However as 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 approach may be used if the RMs used are routinely used in analysis and in the past the information values have provided accurate and precise results.

Limit of Detection (LOD)

Limit of detection (LOD) is defined in many ways and may also be referred to the minimum detectable net concentration or limit of determination/ limit of decision. In its simplest form it is "the lowest concentration that can be measured with reasonable statistical certainty". [7] Generally LODs are calculated using three standard deviations as recommended by the Committee of Environmental Improvement of the American Chemical Society. [8] Therefore LODs are obtained from 3σ and the concentration of the element/ compound determined as described below.

Calibration for Quantification of Results

Up to 5 samples of different concentrations of an element/ compound are prepared and used as RM. Here some results for Fe are given in Table-1. The data in Table-1 shows how a measurement parameter such as peak area varies with Fe concentration. From this data Fig. 2 is plotted and a straight line fitted. The intercept (a) and the slope (b) of the line are given by the equations 2 and 3:

Table-1: Calibration data for Fe synthetic RM.

Fe concentration (mg/kg)	Mean peak area of emitted gamma ray
10.0±0.5	725±36
50.0±2.5	4325±216
100.0±5.0	9406±470
500.0±25.0	45749±2287
1000.0±50.0	120635±6032

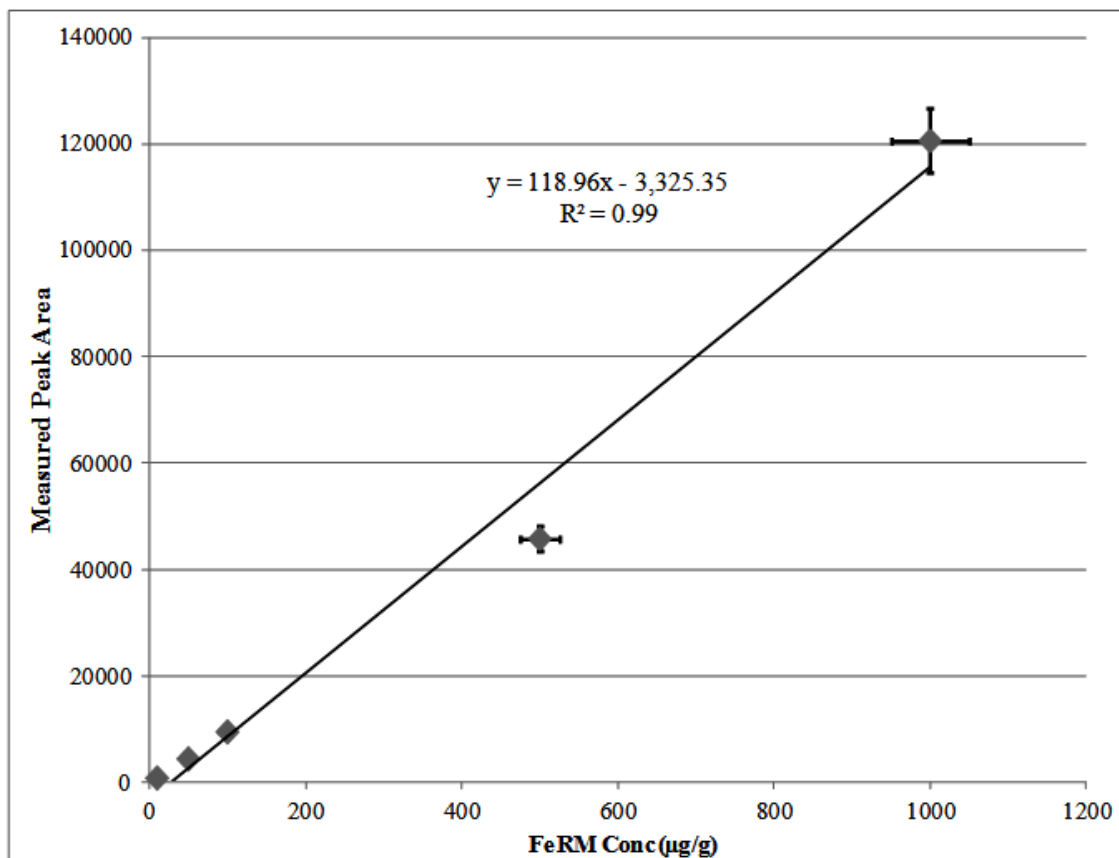


Fig. 2: Calibration plot for Fe.

$$\text{Intercept} = a = \frac{\left(\sum_{i=1}^{i=n} y_i * \sum_{i=1}^{i=n} x_i^2 - \sum_{i=1}^{i=n} x_i * \sum_{i=1}^{i=n} x_i * y_i \right)}{\left(n * \sum_{i=1}^{i=n} x_i^2 - \left(\sum_{i=1}^{i=n} x_i \right)^2 \right)} \quad (2)$$

$$\text{Slope} = b = \frac{\left(n * \sum_{i=1}^{i=n} x_i * y_i - \sum_{i=1}^{i=n} x_i * \sum_{i=1}^{i=n} y_i \right)}{\left(n * \sum_{i=1}^{i=n} x_i^2 - \left(\sum_{i=1}^{i=n} x_i \right)^2 \right)} \quad (3)$$

The standard errors in these parameters are obtained using the formulae given below:

$$SE(a) = \left(\left(\frac{1}{n} \right) + \left(\frac{\bar{x}^2}{\sum_{i=1}^{i=n} (x_i - \bar{x})} \right) \right) \sqrt{\frac{\sum_{i=1}^{i=n} ((b * x_i + a) - y_i)^2}{(n-2)}} \quad (4)$$

$$SE(b) = \frac{\sqrt{\frac{\sum_{i=1}^{i=n} ((b * x_i + a) - y_i)^2}{(n-2)}}}{\sum_{i=1}^{i=n} (x_i - \bar{x})^2} \quad (5)$$

Using the plot in Fig. 2 and equations 1 to 4 the line that best fits the data comes out to be;

$$\text{Peak Area} = 118.96 (\pm 13.10) * [\text{Fe}] - 3325.35 (\pm 0.00) \quad (6)$$

The chi-squared for this plot is 0.99 which shows that this line fits the observed data very well.

The Fe peak areas for the test and blank samples are given in Table-2. These are test data presented here to show how quantitative results are obtained. Here 3 values are given for the peak areas and a mean value is obtained. This is due to the fact that each sample is analyzed in triplicate. Apart from these the different sources of uncertainties are also given in the same unit (percentage). In order to obtain the overall combined uncertainty all uncertainties have to be converted to the same unit (concentration unit or %). Using equation 6 it can be seen that a peak area of 25462 in the test sample corresponds to the Fe concentration [Fe] of 242 µg/g. Similarly the amount of Fe in the blank sample for a peak area of 400 is 31 µg/g giving an overall Fe concentration for the test sample of 211 µg/g. Using a coverage factor of 2 and the data given in Tables 2 and 3 the measurement uncertainty can be obtained to give the amount of Fe in the test sample as 211±41 µg/g while that in the blank is 31±5 µg/g.

From Tables 2 and 3 it can be seen that the uncertainty in the [Fe] of the blank sample is higher than that of the test sample due to the much higher Fe content of the sample. Similarly the LOD for the blank is lower but closer to its Fe content. The closer a value to the LOD for an element/ compound the higher will be its uncertainty and the less reliable its value will be.

The concentrations for all possible elements/ compounds for all samples (test sample, QC material and blank) may be obtained by repetition of the calculations shown above. It should be noted that the number of elements measured in the blank sample should be as few as possible for it to act as a good blank. Moreover the concentration of any element/ compound measured in the blank should also be much lower than that measured in the actual sample. Therefore spec pure reagents are generally used in sample preparation or sampling media such as filters etc are used which should not contribute to the background. However some impurities or species at trace amounts may be present which have to be measured and their amounts subtracted to obtain the actual concentrations.

Quality assurance / quality control (QA/QC)

To prove the validity of the results obtained QC materials such as reference materials (RMs) are

used. Here the data for an RM are shown in Table-4 as an example. In this table recommended values provide by the RM producer along with data obtained during a study are given. The variation in measurements (SD), measurement uncertainties and LODs are also given. An important point to note is that the number of elements listed in the QC table should contain all of the elements quantified in the test sample.

Close examination of Table-4 shows experimental values to be in close agreement with the recommended values. Values for elements that the RM producer has not recommended but has given as information values (Br, Hf, Lu, Sc, Ta, Tb, Th and Tl) are included in this table. In order to see if the results obtained compare well with the recommended values the relative SD (%RSD) can be calculated. If the value of this parameter is ~10% or less for most of the elements studied the results are probably reliable. Another quick indicator of data quality is obtained when ratios of the recommended values are obtained with the observed values. As can be seen from Table-4 these should be as close to 1.0 as possible. From this table it can be seen that around 76% data lies in the range 0.9-1.1 while 92% data lies in the range 0.85-1.15.

Application of t-test

Statistical tools such as t-test may be used to verify similarities between the 2 data sets given in Table 4. When t-test is applied to the results obtained for the RM a value of -0.07 is obtained. At a significance level of 0.05 the value of t for 48 degrees of freedom is 2.01. As the calculated t is lower than this value it shows that the experimental values for these elements do not differ significantly from the recommended values.

Data Evaluation Parameters

In order to carry out more thorough studies and evaluate the results obtained the following parameters may be calculated.

Relative bias

$$R.Bias = \frac{(Value_{Analyst} - Value_{RM})}{Value_{RM}} * 100\% \quad (7)$$

If $R.Bias \leq MAB$ (Maximum Acceptable Bias) implies satisfactory performance and if $R.Bias \geq MAB$ means unsatisfactory performance [9]

MAB values are given by the RM manufacturer and generally have values of 20-25%. These have been obtained and given in Table-5. Scrutiny of the data in Table-5 shows that all of the reported data have $R.Bias < 20\%$ apart from As. The $R.Bias$ for this analyte is $>28\%$ making its value questionable. As these results were obtained using NAA it can be speculated that 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 interferences due to inadequate resolution of the two peaks or limitations with the evaluation software.

Z-Score

$$z - score = \frac{(Value_{Analyst} - Value_{RM})}{\sigma} \quad (8)$$

where $\sigma = 12.5\%$ of the consensus/assigned value.[9]

If $|z-score| \leq 2$ satisfactory performance
 $2 < |z-score| < 3$ questionable performance
 and $|z-score| \geq 3$ unsatisfactory performance

Z-Scores were calculated and are also given in Table-5. From this data once again it can be seen that all of the reported data has z-scores less than 2 apart from As which has a z-score >2 but <3 making its value questionable. Table 5 also shows that all reported results have acceptable z-scores. This shows that the procedures employed in obtaining the given results are good and produce accurate and precise results. However care should be exercised when measuring the As concentration in a sample

u-Test

$$u - Test = \frac{|Value_{Analyst} - Value_{RM}|}{\sqrt{Unc_{Analyst}^2 + Unc_{RM}^2}} \quad (9)$$

If $u < 2.58$ it implies satisfactory performance for a level of probability at 99%. [9]

U-Test values were calculated and are given in Table 5. These fulfill the criteria for good reliable results as $u < 2.58$ for all of reported data including As. Therefore it can be seen that no one parameter shows the reliability of a value as u-test shows that As value is also reliable whereas $R.Bias$ and z-score show the data for this analyte to be questionable.

Table-2: Estimation of measurement uncertainty. (Data cited at 95% confidence interval).

Sample	Fe Peak Area			Mean	SD	%SD	Unc _{CPA}	Uncertainty Budget (%)				Combined Unc (%)	
	Value 1	Value 2	Value 3					Unc _{CB}	Unc _{WC}	Unc _{CV}	Unc _{CD}		Unc _{CRM}
Test Sample	25210	25437	25739	25462	265	1.04	0.63	4.00	0.50	1.00	1.00	2.00	9.74
Blank	385	423	392	400	20	5.06	5.00	4.00	0.50	1.00	1.00		16.59

Table-3: Fe concentration and LOD (mg/kg) of test and blank samples. (Data cited at 95% confidence interval).

Sample	Peak Area	[Fe]=(Peak Area+3325.35)/118.96 (mg/kg)	Unc (mg/kg)	3 Sigma (%)	LOD (mg/kg)
Test Sample + Blank Sample	25462	242	24	5.00	12.10
Blank	400	31	5	8.00	2.51
Test Sample	25062	211	41	9.43	19.91

Table-4: Elemental composition of QC material at 95% confidence interval.

Element	Laboratory Values (mg/kg)					Recommended Values (mg/kg)		Ratio of Recommended /Lab Values
	Mean	Unc	RSD (%)	SD	LOD	Mean	SD	
Al	44336	4440	7.4	3268	1215	51800	6475	1.17
As	8.24	1.26	10.7	0.88	0.25	11.50	1.44	1.40
#Br	216	66	8.9	19.31	113.96	224.00	28.00	1.04
Ce	63.02	15.96	6.0	3.81	1.30	61.10	7.64	0.97
Co	8.87	2.14	6.7	0.59	0.30	9.20	1.15	1.04
Cr	74.00	16.05	5.3	3.87	3.26	74.40	9.30	1.01
Cs	3.65	0.54	4.9	0.18	0.45	3.73	0.47	1.02
Eu	0.97	0.30	9.3	0.09	0.06	1.08	0.13	1.11
Fe	26081	1388	4.2	1099	363	26300	3288	1.01
#Hf	5.75	0.90	3.5	0.24	0.24	6.23	0.78	1.08
K	19057	5988	11.5	2197	3453	20000	2500	1.05
La	28.55	5.82	8.7	2.52	1.97	30.20	3.78	1.06
#Lu	0.28	0.11	10.7	0.03	0.02	0.31	0.04	1.11
Mn	332	46	12.9	43	2	356	45	1.07
Na	23756	1891	3.7	890	190	23800	2975	1.00
Rb	73.63	10.36	9.5	7.02	24.35	82.00	10.25	1.11
Sb	1.34	0.21	10.4	0.14	0.30	1.34	0.17	1.00
#Sc	8.14	1.23	3.7	0.26	0.09	8.32	1.04	1.02
Sm	4.62	0.41	6.5	0.25	0.07	4.94	0.62	1.07
#Ta	0.93	0.26	10.8	0.10	0.05	0.97	0.12	1.04
#Tb	0.70	0.33	5.7	0.04	0.03	0.63	0.08	0.90
#Th	8.30	1.27	4.8	0.37	0.22	8.89	1.11	1.07
V	63.92	10.43	6.6	4.20	16.82	73.00	9.13	1.14
#Yb	1.94	0.57	9.3	0.18	0.25	2.08	0.26	1.07
Zn	151	17	9.0	13.46	3.60	140.60	17.58	0.93

Given as information values by the RM producer

Table-5: Evaluation of data obtained for QC material (Reference Material).

Element	Rel Bias (%)	z-score	u-test	Trueness		Precision		Final Score
				A1	A2	Acceptance	P (%)	
Al	-14.41	-1.15	-0.95	7464.17	20256.42	A	16.02	A
As	-28.39	-2.27	-1.71	3.26	4.94	A	19.78	A
#Br	-3.67	-0.29	-0.11	8.21	185.77	A	33.19	A
Ce	3.14	0.25	0.11	1.92	45.64	A	28.24	A
Co	-3.55	-0.28	-0.13	0.33	6.27	A	27.15	A
Cr	-0.53	-0.04	-0.02	0.40	47.86	A	25.03	A
Cs	-2.25	-0.18	-0.12	0.08	1.85	A	19.48	A
Eu	-10.17	-0.81	-0.34	0.11	0.84	A	33.12	A
Fe	-0.83	-0.07	-0.06	219.14	9207.19	A	13.59	A
#Hf	-7.76	-0.62	-0.41	0.48	3.06	A	19.99	A
K	-4.71	-0.38	-0.15	942.80	16742.13	A	33.82	A
La	-5.45	-0.44	-0.24	1.65	17.91	A	23.92	A
#Lu	-9.58	-0.77	-0.25	0.03	0.31	A	42.69	N
Mn	-6.87	-0.55	-0.38	24.46	164.63	A	18.61	A
Na	-0.18	-0.01	-0.01	43.99	9094.42	A	14.82	A
Rb	-10.21	-0.82	-0.57	8.37	37.60	A	18.82	A
Sb	-0.06	0.00	0.00	0.00	0.70	A	20.26	A
#Sc	-2.20	-0.18	-0.11	0.18	4.15	A	19.58	A
Sm	-6.54	-0.52	-0.44	0.32	1.92	A	15.36	A
#Ta	-3.96	-0.32	-0.13	0.04	0.74	A	30.48	A
#Tb	10.71	0.86	0.20	0.07	0.87	A	48.60	N
#Th	-6.63	-0.53	-0.35	0.59	4.36	A	19.79	A
V	-12.44	-1.00	-0.66	9.89	35.75	A	20.55	A
#Yb	-6.57	-0.53	-0.22	0.14	1.62	A	32.02	A
Zn	7.13	0.57	0.41	10.02	62.78	A	16.76	A

Given as information values by the RM producer

Trueness

For results to be accurate the requirement is [9]

$$A1 \leq A2$$

where

$$A1 = |Value_{Analyst} - Value_{RM}| \quad (10)$$

$$\text{and } A2 = 2.58 * \sqrt{Unc_{Analyst}^2 + Unc_{RM}^2} \quad (11)$$

The values of A1 and A2 were calculated and are given in Table-5. From these results it can be seen that all of the data fulfills the expressions $A1 \leq A2$ meaning that the trueness of accuracy criteria is fulfilled.

Precision

To check the precision of the data the following parameter is calculated: [9]

$$P = \sqrt{\left(\left(\frac{Unc_{Analyst}}{Value_{Analyst}} \right)^2 + \left(\frac{Unc_{RM}}{Value_{RM}} \right)^2 \right)} * 100\% \quad (12)$$

If $P \leq LAP$ (Limit of Acceptable Precision) implies satisfactory performance

LAP data are given by the RM manufacturer and generally have magnitudes of 20-25%. However LAPs may be as high as 40% in some cases. The parameter P has been obtained for all of the elements determined in the RM sample and are given in Table. From these results it can be seen that 23 of the 25 elements determined in the RM sample have $P \leq MAB$, only Lu and Tb have $P > 40\%$. This may be due to the higher reported uncertainties for these elements which can be reduced by greater care in carrying out analysis as well as using RMs with lower uncertainties for these elements.

Acceptance Criteria

In order to reach a final decision about each value in a data set the following criteria are used. If any of the z or u score criteria are not fulfilled then the result is declared "Not Acceptable". However if all criteria are fulfilled but either trueness or precision criteria is not fulfilled then a further check is applied i.e. the reported result relative bias (R.Bias) is compared with the maximum acceptable bias (MAB) as defined by the RM producer. If $R.Bias \leq MAB$, the final score will be "Warning". "Warning" reflects two situations; 1) the result has a small measurement uncertainty; but its bias is still within MAB or 2) a result close to the assigned property

value is reported, but the associated uncertainty is large. If $R.Bias > MAB$ the result will be "Not Acceptable". Evaluation of the results for the RM sample using the treatment outlined above provides the outcomes given in Table-5. Therefore only the results for Lu and Tb fall into the "Warning" category, while the data for the remaining 23 elements are all classified as acceptable. [9].

Laboratory Classification

RM manufacturers, such as the International Atomic Energy Agency (IAEA), uses the following criteria to evaluate the performance of laboratories which participate in any intercomparison or proficiency test (PT) exercise: [10]

Group 1: laboratories scoring $|z\text{-score}| < 3$ for $\geq 90\%$ of the data;

Group 2: laboratories scoring $|z\text{-score}| < 3$ for 75% to $< 90\%$ of the data;

Group 3: laboratories scoring $|z\text{-score}| < 3$ for 50% to $< 75\%$ of the data;

Group 4: laboratories scoring $|z\text{-score}| < 3$ for $< 50\%$ of the data

If the above criteria are used for self evaluation by a laboratory or for an analytical procedure, then as all of the data given in Table-4 and 5 have $|z\text{-score}| < 3$ therefore the laboratory is placed in Group 1. Moreover taking into account all of the acceptance criteria it can be seen from Table-5 that 23 of the 25 results reported i.e. 92% are acceptable with only the results for Lu and Tb being deemed unsatisfactory.

Graphical representation of QA/QC results

Generally it is better to show results graphically as plots show most trends more clearly and are easier to read. Here various parameters, as given in Tables 4 and 5, have been plotted to highlight this point. [10-19] In Fig. 3 the recommended and observed laboratory values have been plotted side by side as bars to show direct comparison between the two data sets. This is shown as a log plot to include elements with a large range of concentrations. The uncertainties in both data sets have also been plotted as error bars. From this plot it can be seen that the bars for the recommended and laboratory values for each element have very similar lengths. Table-4 and Fig. 3 are the simplest ways of comparing RM data with observed results and can point out outliers and significantly different data points at a glance.

In Fig. 4 the recommended values have been plotted against the observed values for the RM sample. This is another simple way of presenting the results without much data manipulation. As can be seen from this figure, all data points lie on the $y=x$ line with intercept of zero. This shows good agreement between the 2 datasets. Such plots are generally presented as log log plots to take into account the large concentration ranges of elements present in the RMs. Uncertainties cited by the RM producer and those measured are also plotted to show any variations in data.

Another graphical method of data presentation is by plotting the ratios of the recommended to the laboratory values. This has been done in Fig. 5. These values were given in Table-4 but in this plot it can be seen that the elements Al, As, Eu, Rb, Tb and V lie outside the $\pm 10\%$ range. This parameter shows the questionable character of As which is underestimated significantly in this study. Moreover Tb is over-estimated as it has the lowest ratio.

Graphically data can be presented by utilizing equations 7 to 9 and plotted the Relative Bias, the z-scores and the u-test values. This has been

done in Figs. 6 to 8 respectively. Therefore in Fig. 6 the Relative Bias (Rel.Bias%) has been plotted for the RM for all the elements measured. From this figure it can be seen that the values of this parameter are generally negative in magnitude which means that the observed values are less than the recommended values suggesting slight under-estimation. This feature is more evident for the elements As and Tb for reasons mentioned earlier. In Figs. 7 and 8 the z-scores and the u-Test values have been plotted. From these figures it can be seen that As has the highest magnitude of both these parameters. However the magnitudes of both these parameters lie within the prescribed ranges.

From Figs. 3 to 8 the same results are presented in various ways to distinguish between reliable and less reliable results. The same results are presented in Tables 3 and 4. From these plots and tables it can be seen that the data obtained for the QC material RM is in very good agreement with the recommended values. Hence the methodology used to obtain the results reported in Table-4 provided reliable results giving the analyst confidence in the reported results.

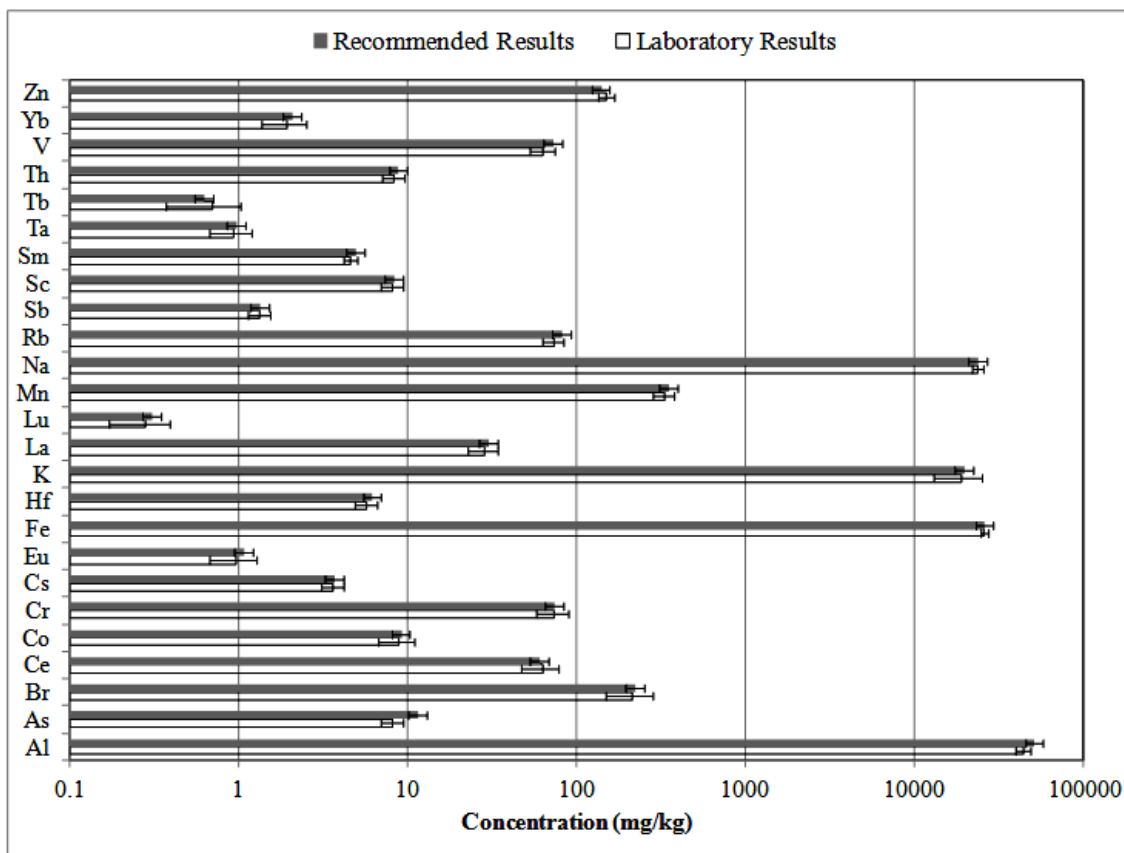


Fig. 3: Plot of recommended and laboratory values for RM sample.

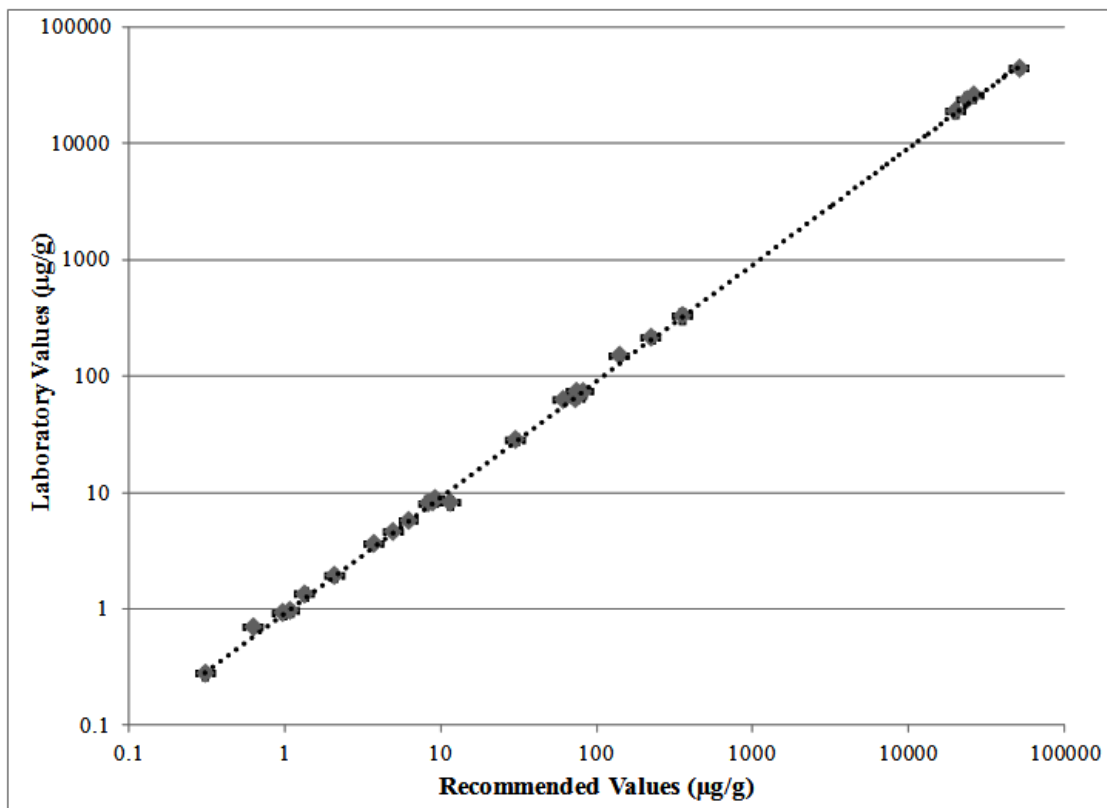


Fig. 4: Comparison of recommended data with the laboratory results for RM sample.

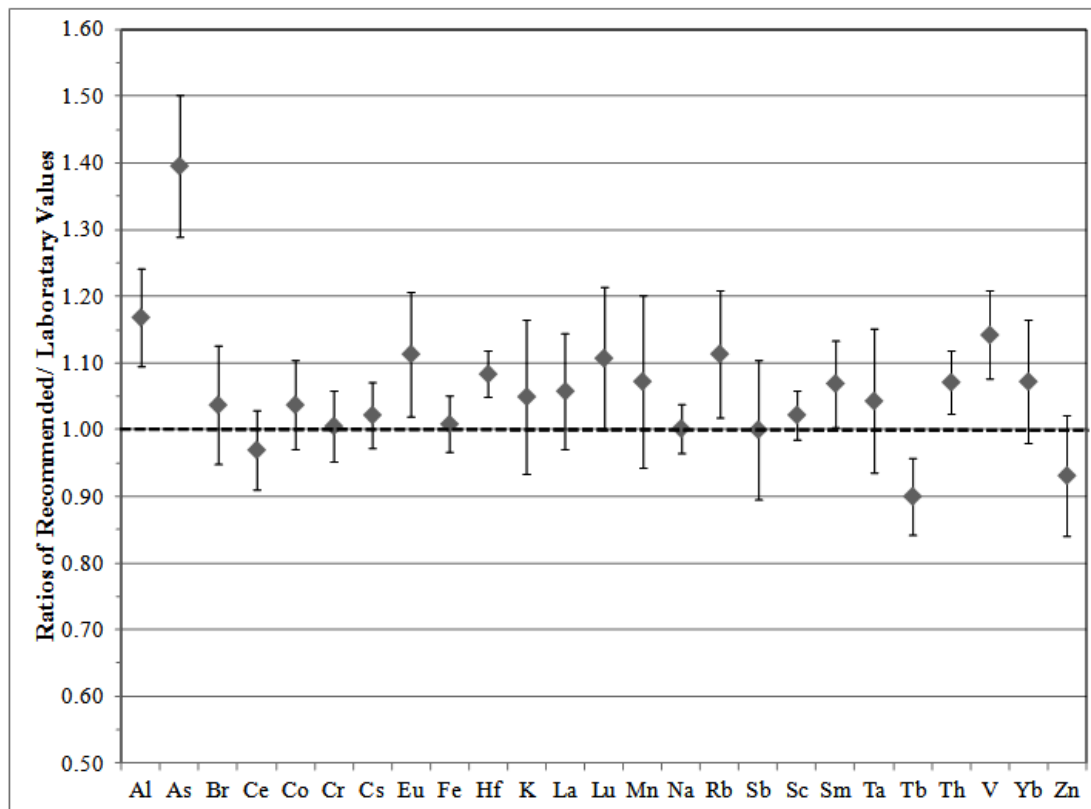


Fig. 5: Plot of ratios of recommended/ laboratory values for RM sample.

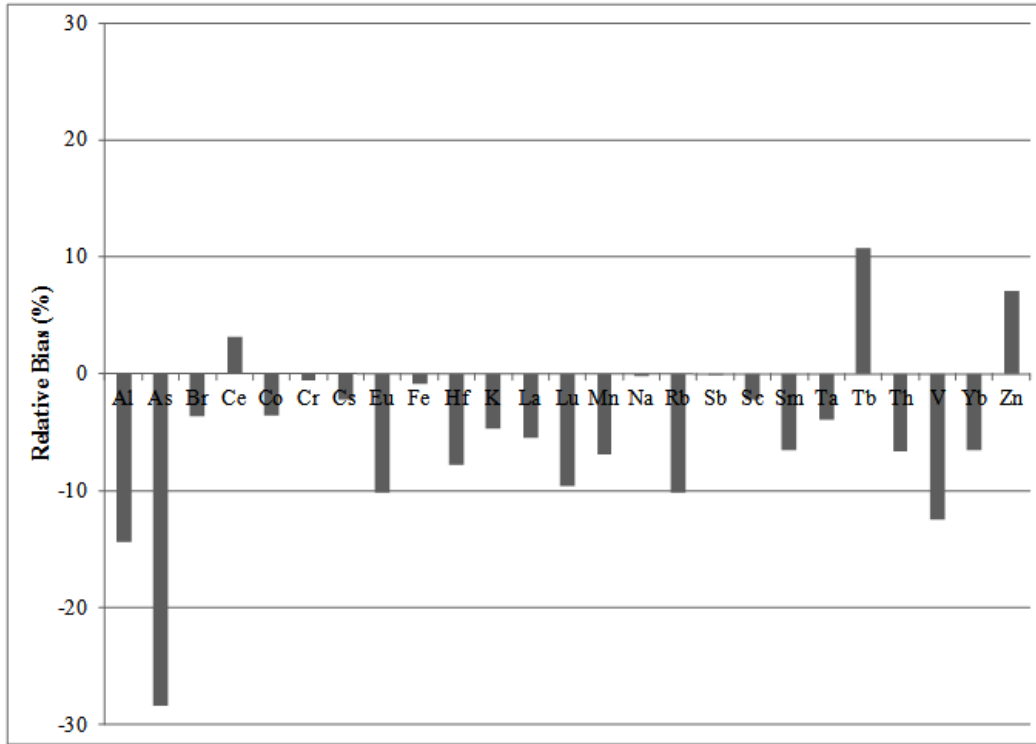


Fig. 6: Relative bias plot for RM sample.

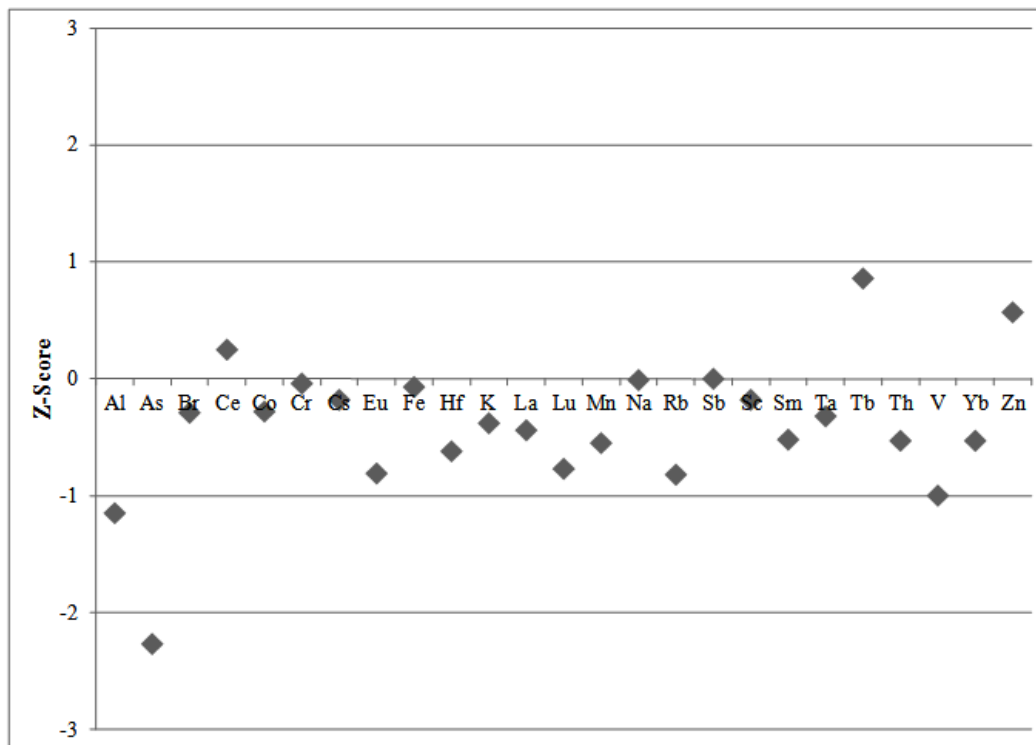


Fig. 7: Z-scored plot for RM sample.

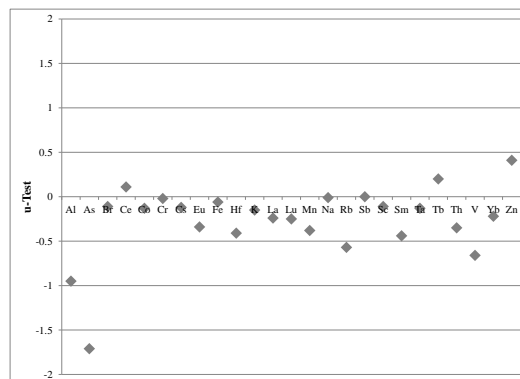


Fig. 8: u-Test plot for RM sample.

Conclusion

The information presented in this paper shows the importance of understanding analytical data and how to present them so that the reader can easily understand how they have been obtained. It also shows the significance of simple evaluation tools which can be used routinely to evaluate the results obtained and provide confidence in the reported results. Such tools can be used to devise and test new analytical procedures as well as test and evaluate the performance of individual laboratories or analysts.

References

1. S. Waheed, N. Siddique and J. H. Zaidi, *Journal of Radioanalytical and Nuclear Chemistry*, **289**, 765, (2011).
2. N. Siddique and S. Waheed, *Journal of Radioanalytical and Nuclear Chemistry*, **291**, 817 (2012).
3. N. Siddique, S. Waheed and Y. Faiz, *Journal of Radioanalytical and Nuclear Chemistry*, **291**, 919 (2012).
4. N. Siddique, Sabiha-Javied, S. Waheed and M. Tufail, *Journal of Radioanalytical and Nuclear Chemistry*, **292**, 445 (2012).
5. [http://www.pnac.org.pk/info/Accreditation%20Scopes/Finalized%20Scopes%20\(Feb%202007\)/PINSTECH%20Lab,%20Nilore.pdf](http://www.pnac.org.pk/info/Accreditation%20Scopes/Finalized%20Scopes%20(Feb%202007)/PINSTECH%20Lab,%20Nilore.pdf)
<http://www.pnac.org.pk/index.php?PageId=87>
6. International Standard ISO/IEC 17025, Second edition 2005-05-15 General Requirements for the Competence of Testing and Calibration Laboratories ISO, Geneva Switzerland
7. Quantifying Uncertainty in Nuclear Analytical Measurements, Eurachem/ Citac Guide, (2000)
8. R. J. Mesley, W. D. Pocklington and R. F. Walker, *Analyst*, **116**, 975 (1991).
9. A. Shakhshiro, A. Trinkl, A. Torvenyi, E. Zeiller, T. Benesch, U. Sansone. (2006) IAEA/AL/168, Report on the IAEA-CU-2006-06 Proficiency Test on the determination of major, minor and trace elements in ancient Chinese ceramic, Seibersdorf, Austria, November 2006
10. N. Siddique, S. Waheed, M. Daud, A. Rahman and S. Ahmad, *Journal of Radioanalytical and Nuclear Chemistry*, **274**, 181 (2007).
11. S. Waheed, M. Waseem, A. Rahman and S. Ahmad, *Geostandards Newsletter*, **25**, 137 (2001).
12. S. Waheed, S. Ahmad, A. Rahman and I. H. Qureshi, *Journal of Radioanalytical and Nuclear Chemistry*, **250**, 97 (2001).
13. S. Waheed, A. Rahman, M. Daud, J. H. Zaidi and S. Ahmad, *Radiochimica Acta*, **92**, 939 (2004).
14. N. Siddique, A. Rahman, S. Waheed, M. Wasim, M. Daud and S. Ahmad, *Journal of Radioanalytical and Nuclear Chemistry*, **268**, 579 (2006).
15. S. Waheed, A. Rahman, N. Siddique, S. Ahmad and M. Rossbach, *Accreditation and Quality Assurance*, **12**, 311 (2007).
16. S. Waheed, N. Siddique, M. Arif, I. Fatima, N. Khalid, S. Rahman, M. Daud and M. Wasim, *Journal of Radioanalytical and Nuclear Chemistry*, **277**, 539 (2008).
17. N. Siddique, A. Rahman, S. Waheed, M. Wasim, M. Daud and S. Ahmad, *Journal of the Chemical Society of Pakistan*, **31**, 622 (2009).
18. S. Waheed, A. Rahman, N. Siddique and S. Ahmad, *Geostandards and Geoanalytical Research*, **31**, 133, (2007).
19. N. Siddique and S. Waheed, *Journal of the Chemical Society of Pakistan*, **31**, 916, (2009).