

## CERTIFIED REFERENCE MATERIALS FOR ANALYTICAL QUALITY CONTROL IN NEUTRON ACTIVATION ANALYSIS

Wee Boon Siong\*, Abdul Khalik Hj. Wood, Mohd. Suhaimi Hamzah, Shamsiah Abdul Rahman, Md. Suhaimi Elias, and Nazaratul Ashifa Abd. Salim

*Malaysian Institute for Nuclear Technology Research (MINT)  
Bangi, 43000 Kajang, Selangor, Malaysia.*

**Keywords:** certified reference materials, analytical quality control, neutron activation analysis.

### **Abstract**

Analytical quality control in neutron activation analysis (NAA) requires the use of certified reference materials (CRM) in order to produce reliable analytical results. It is essential to evaluate the performance of NAA method when analyzing various sample matrices. Therefore, the CRM selected for an analysis should be suitable for the type of samples. There are many aspects such as concentration range, matrix match, sample size, and uncertainty, which need to be considered when selecting a suitable CRM. Eventually, results of analysis of CRM were plotted into control charts in order to evaluate the quality of the data. This is to ensure that the results are within the 95% confidence interval as stipulated in the certificate of CRM. Thus, this article aims to discuss the uses of certified reference materials for quality control purposes in NAA involving various sample matrices.

### **Abstrak**

Bahan rujukan piawai adalah berguna dalam kawalan mutu analisis dalam analisis pengaktifan neutron untuk memperolehi keputusan analisis yang boleh dipercayai. Ia juga penting dalam menilai keputusan kaedah NAA semasa menganalisa pelbagai bahan sampel. Oleh yang demikian, bahan rujukan piawai yang dipilih hendaklah bersesuaian dengan jenis sampel yang dikaji. Terdapat beberapa faktor yang perlu dipertimbangkan semasa memilih bahan rujukan piawai seperti julat kepekatan, kesesuaian matriks, saiz sampel, dan ketidakpastian. Keputusan analisis bahan rujukan piawai diplotkan dalam carta kawalan untuk menilai kualiti data. Ini adalah untuk memastikan keputusan adalah dalam lingkungan 95% confidence interval berbanding dengan sijek bahan rujukan piawai. Kertas kerja ini bertujuan untuk membincangkan kegunaan bahan rujukan piawai dalam kawalan mutu dalam analisis pengaktifan neutron yang melibatkan pelbagai jenis sampel.

### **Introduction**

Chemical measurement requires data to be reliable in order to produce a correct interpretation when the data is used for specific purposes such as pollution studies, forensic science and human health. Therefore, the data from various chemical measurement techniques needs to go through analytical quality control measure. Eventually, certified reference materials (CRM) is used in the chemical measurement so as to improve the quality of the results. According to the ISO Guide 30, a CRM is defined as reference material, accompanied by a certificate, one or more of whose property values are certified by a procedure which establishes its 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 [1]. There are many important uses of CRM namely for method validation, measurement uncertainty, verification of a method, instrumental calibration, quality control, traceability, and production of secondary reference materials [2].

In neutron activation analysis (NAA), CRM is an important part of the analytical procedure. This is because chemical measurement data requires proper analytical quality control in order to ensure the data is reliable and accurate. The CRM required for NAA can be obtained from institution around the world such as National Institute of Standards and Technology (NIST), and Institute for Reference Materials and Measurements (IRMM). These institutions produce CRM through a stringent protocol to properly characterize and determine the certified values of the CRM and certificate and report can be issued. The CRM produced are traceable to these institutions. However, much effort has been taken to ensure that the CRM produced from these institutions could produce a key link in the traceability chain [3]. Thus, utilizing CRM which has traceability to international standards will ensure that analytical results are reliable and comparable.

Upon discussing the advantages of CRM, it has been used routinely in NAA as analytical quality control material in order to ascertain the reliability of the result which is important to chemist and end-users. The analysis of CRM, however, will provide information on the deviation of the analytical results from certified or consensus values. There are many reasons contribute to the deviation of measured values to certified or consensus values, for example, the spectral interferences, the performance of the analyst, the performance of the equipment, absolute quantity of the analyte and the fitness of the reference materials [4]. The result obtained from the analysis can then be presented in the form of control charts for efficient operational management of NAA procedure [4]. Therefore, this paper aims to present the data from the analysis of selected CRM using NAA and to evaluate the results using control charts as a tool for quality control.

### Experimental

A set of CRM selected for this experiment was chosen based on their matrixes which are common to our routine analysis work. The CRM analyzed are NIST SRM 1633a (Coal Fly Ash), NIST SRM 1632c (Bituminous Coal), NIST SRM 1646a (Estuarine Sediment), and NIST SRM1566b (Oyster tissue). Apart from CRM, other reference materials analyzed include IAEA Soil 7, IAEA 140/TM (Seaweed), IAEA 312 (Soil). In general, the CRM and standard solutions for analysis were weighted (0.1 – 0.5 g) in duplicates into irradiation vials. Empty vials were also analysed as blank for error correction. Soon after the preparation steps, all standard solutions and CRM were irradiated at the MINT TRIGA Mark II reactor at 750 kW with neutron flux in the order of  $10^{12}$  n·cm<sup>-2</sup>·s<sup>-1</sup>. The irradiation time was ranged from 1 minute to 6 hours with cooling for 10 minutes to 4 days prior to counting using HPGe  $\gamma$ -ray spectrometry systems equipped with multi-channel analyzer. The counting time was ranged from 5 minutes to 1 hour and counting geometry was set at 9 – 12 cm from the  $\gamma$ -ray detector. The detector was calibrated as described in previous literature [5]. The analytical results were evaluated and plotted as control charts.

### Results and Discussions

In the analysis of samples, the used of control charts is essential to obtain information regarding the trend and deviations occurred at a certain period of time. There are many ways to create a control chart by selecting the type of parameter to be displayed. For instance, in most common cases, Yaxis is used for showing the concentration of the element analyzed and x-axis is the measurement date. An example is as shown in Fig. 1 where IAEA 312 is analyzed for uranium concentration. In the Fig. 1, the results for uranium concentration of IAEA 312 obtained were assumed to be normally distributed were shown in control charts whereby the horizontal line indicates the mean, acceptance limit (mean  $\pm$  1 $\sigma$ ), warning limit (mean  $\pm$  2 $\sigma$ ), and action limit (mean  $\pm$  3 $\sigma$ ). The mean and  $\sigma$  (standard deviation) values used in this control chart were estimated based on results obtained from previous analysis of IAEA 312. This is aimed for internal quality control of the analytical results obtained over a long period. Whenever the analytical results of uranium are found to be higher or lower than the action limit it will be rejected and reanalyzed. However, analyst will be informed and warned if the results go beyond upper or lower warning limit. Proper corrective action could be taken to mitigate this problem.

Another way of showing the control chart is by using the z-score at Y-axis against the elements at X-axis. This is type of control chart is useful to show how each element in the CRM deviates from the certified or consensus values (Fig. 2). The z-score of an element concentration is computed based on the following equation [4]:

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

where  $x$  is the analytical result;  $c$  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 is based on counting statistics whilst the uncertainty of the certified value is based on the certificate. However, the Horwitz function is used to estimate the uncertainties of information values in the certificates [6]. 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. The analysis of the selected CRMs showed that most results are within the acceptance criteria. However, for biological sample namely NIST SRM 1566b, there was a systematic bias for most of the elements analyzed. The problem might be related to the presence of moisture content and matrix element which affects the overall concentration of the elements. In this case, the measured values were found out to be 6 – 9% lower than the certified values except for the elements, K, Na, and Se. The interference from matrix elements such as K and Na after irradiation will compromise the counting of other elements which has lower activities and resulted in counting error. This can be minimized by allowing the interfering radionuclides to decay for a

longer period. Thus, longer counting time would be required to detect elements of interest which have lower activities. Recently, advanced methods in gamma-spectrometry to overcome the problem of interfering radionuclides have been described [7]. From the control charts showed, it is evident that geological samples such as soil, fly ash, sediments are more easily determined by NAA as the effects of moisture and matrix is less. On the other hand, other interfering factor such as detector calibration, geometry of counting, neutron flux variation and dead-time may affect the results of the analysis [8].

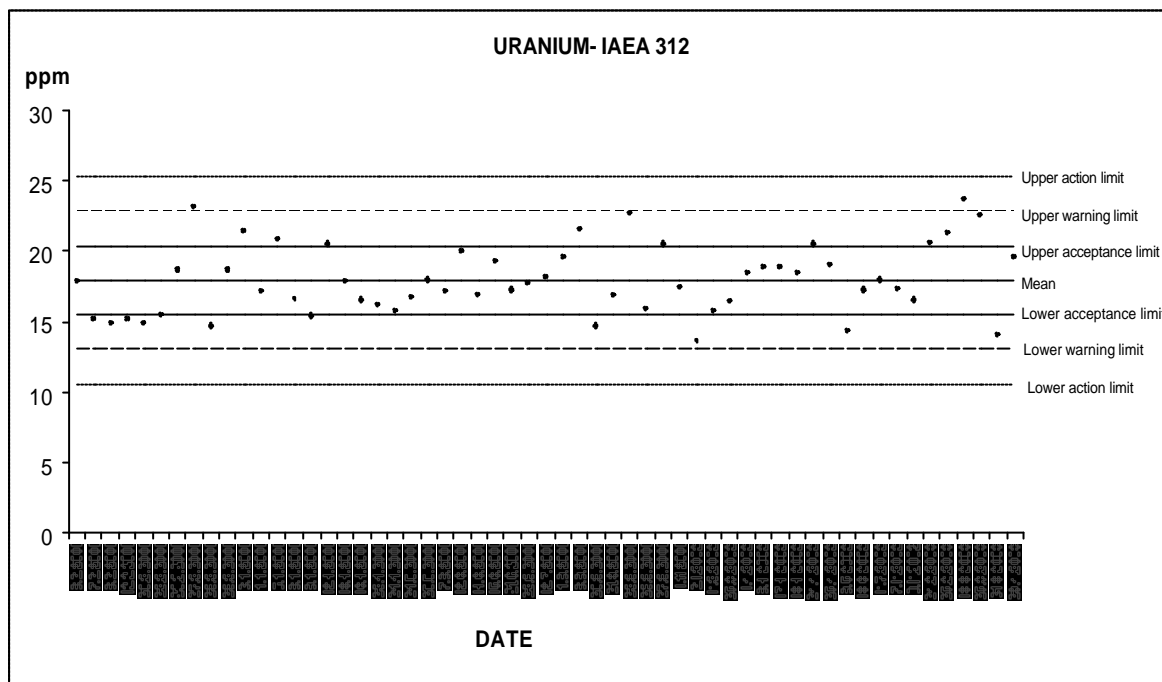
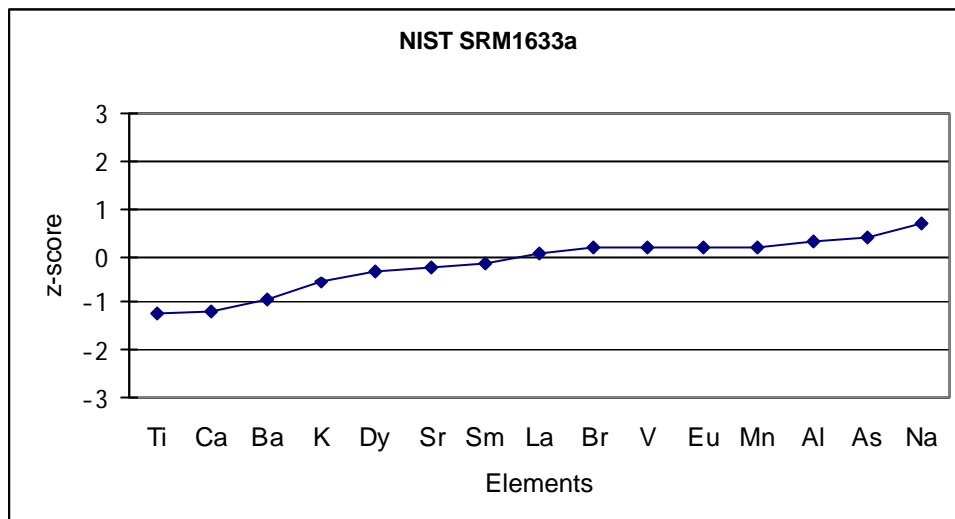


Fig. 1: Control chart for the determination of U concentration in IAEA 312.

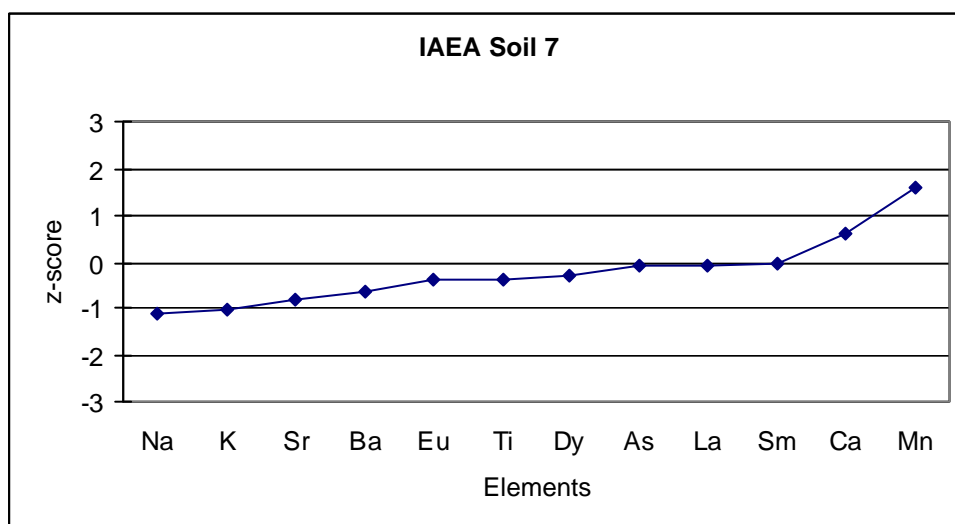
The use of CRMs in quality control of NAA method has to take into account the suitability of the CRMs which is fit for the purpose based on client and analytical requirements. There are many factors that need to be considered such as concentration range, sample size, matrix match, homogeneity, measurement uncertainty, and elements of interest. In most cases, recommendation stated in the certificate is followed as it has been verified and tested with confidence. For instance, the amount of NIST SRM 1633b recommended to be used is 250 mg dry weight as the certified values were determined based on this criterion. However, different CRM has different recommendation of use. For example, the amount recommended for NIST SRM 1646a is 500 mg dry weight. By following the recommendation in the certificate, it is to ensure that the values determined are relevant to the certified values stated in the certificate of analysis. An analyst has to determine the type of CRM appropriate for each type of sample analyzed so that the matrix of the CRM is identical to the sample analyzed. This is to ensure that a better indication on the accuracy and precision of the results could be obtained.

### Conclusion

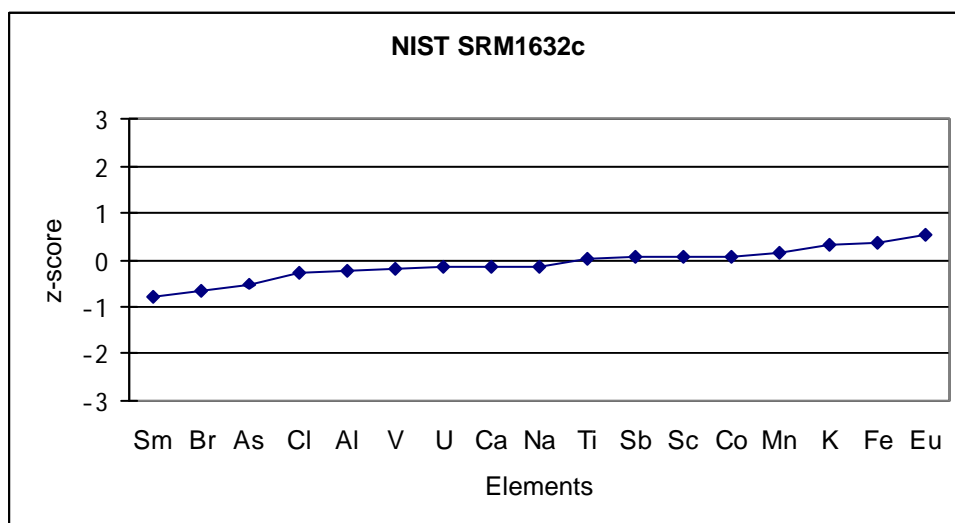
The use of CRM in NAA has proved to be a good way to improve the overall reliability of the results produced from each analysis. This is because quality control measures could be taken to overcome problems related to systemic or random errors arise during the analysis of CRMs. Besides, element concentration data from the analysis of CRMs could be kept and analyzed from time-to-time in order to evaluate the performance of the method used as well as to maintain the quality of the results produced. This is due to the fact that the laboratory is providing analytical service to client and therefore it is the responsibility of the laboratory to give results that is fit for the intended purposes. This is also in agreement with the implementation of quality system in the laboratory where analytical results are of great importance to show the performance of the laboratory.



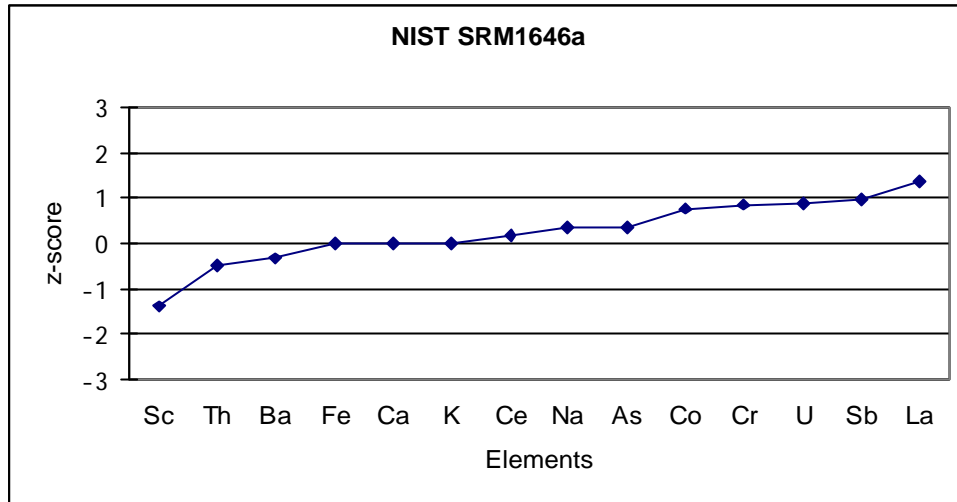
(a)



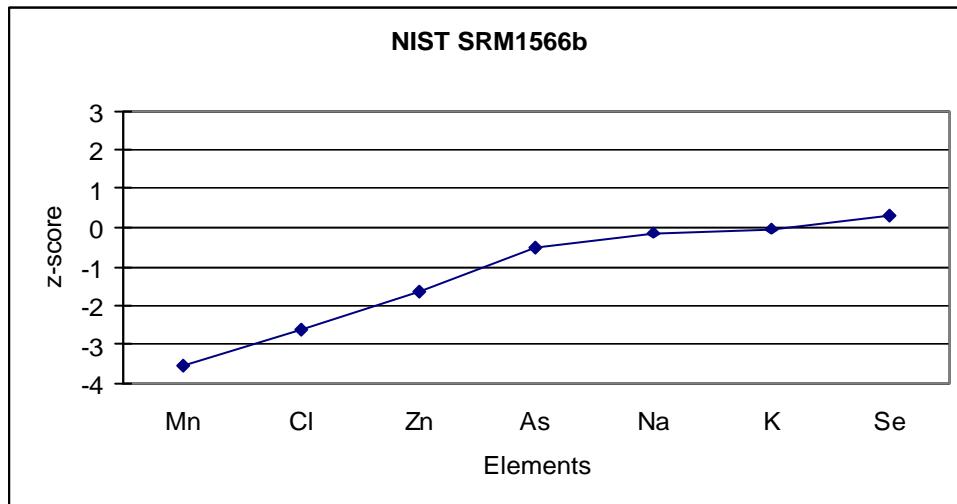
(b)



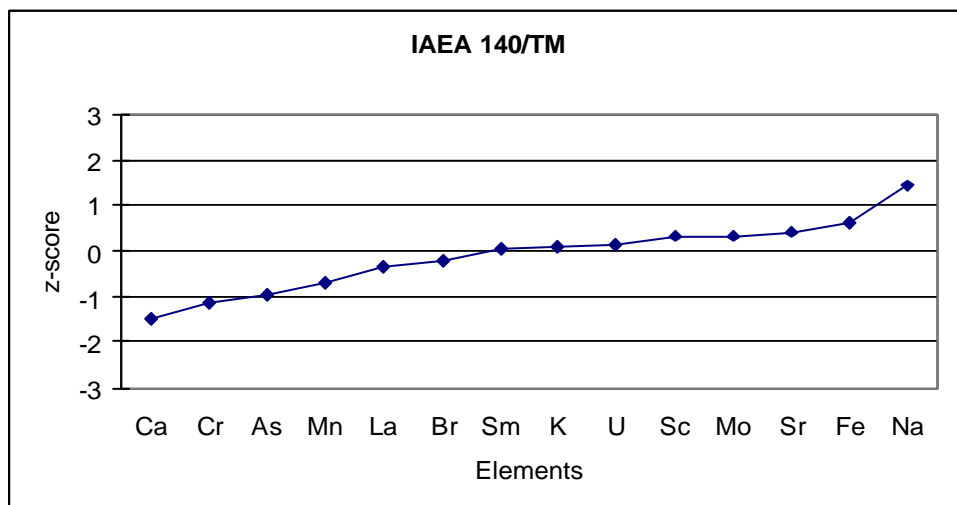
(c)



(d)



(e)



(f)

Fig.2: Control charts (a – f) showing the z-scores of the reference materials analyzed in this work.

### Acknowledgements

The authors would like to extend their gratitude and thanks to the management of MINT for approval of funding to this study. Special thanks also to the staff of Analytical Chemistry Laboratory for their continuous endeavor throughout the tenure of this study.

### References

1. ISO Guide 30 (1992). Terms and Definitions used in connection with reference materials, ISO, Geneva.
2. R. Walker and I. Lumley (1999). Pitfalls in terminology and use of reference materials. *Trends Anal. Chem.* 18, 594 – 616.
3. B. King (1997). Traceability of chemical analysis. *Analyst* 122, 197 – 204.
4. P. Bode and C.P. van Dijk (1997). Operational management of results in INAA utilizing a versatile system of control charts. *J. Radioanal. Nucl. Chem.* 215, 87 – 94.
5. W.B. Siong, H.M. Dung, A.K. Wood, N.A.A. Salim and M.S. Elias (2006). Testing the applicability of k0-INAA at the MINT's TRIGA MK II reactor. *Nucl. Instr. & Meth. A* 564, 716 – 720.
6. M. Thompson (2000). Recent trends in inter-laboratory precision at ppb and sub-ppb concentrations in relation to fitness for purpose criteria in proficiency testing. *Analyst* 125, 385 – 386.
7. R. Zeisler, E.A. Mackey, G.P. Lamaze, T.E. Stover, R.O. Spatz and R.R. Greenberg (2006). NAA methods for determination of nanogram amounts of arsenic in biological samples. *J. Radioanal. Nucl. Chem.* 269, 291 – 296.
8. J. Kucera, P. Bode and V. Stepanek (2000). The 1993 ISO Guide to the expression of uncertainty in measurement applied to NAA. *J. Radioanal. Nucl. Chem.* 245, 115 – 122.