Transactions of the Korean Nuclear Society Spring Meeting
Jeju, Korea, May 18-19, 2023

Participation in IAEA Proficiency Test Exercise on Determination of Elements in Clay and Plant samples through INAA using HANARO Reactor

K. B. Dasari[a,b], H. Cho[c], S. P. Hong[b], J. H. Moon[b], G. M. Sun[b*]
[a]*The Research Institute of Natural Science, GNU, Jinju 52725, Republic of Korea*
[b]*Hanaro Utilization Division, KAERI, Daejeon 34057, Republic of Korea*
[c]*Division of Chemical and Biological Metrology, KRISS, Daejeon 34113, Republic of Korea*
(Corresponding Author Email: gmsun@kaeri.re.kr)*

1. Introduction

Quality assurance and quality control of analytical results have become the high market demand in the global analytical laboratories development. Accurate and reliable analytical data is one of the requirements for an analytical laboratory to get recognition from customers. The best way to check the capabilities and validation of analytical results by comparison with other laboratories is through participation in proficiency testing (PT)[1]. PT is an analytical quality assessment tool, also known as external validation. It provides the laboratory with an external independent assessment of its test results by comparing it to an assigned value and other peer laboratories.

The comparator instrumental neutron activation analysis (INAA) methodology was established for high-quality analytical results and reference materials development using the HANARO research reactor. INAA provides high accuracy and sensitivity, does not require complicated sample preparation, and can be measured many elements (>40) including rare earth elements simultaneously. In addition, it has been recognized as a primary ratio method by the Consultative Committee on Amount of Substance (CCQM) along with an isotope dilution mass spectrometry (IDMS), and are used actively in the field of reference materials development [2].

In the present study, INAA laboratory from KAERI participated in the inter-laboratory comparative test (PTNATIAEA20) conducted by the International Atomic Energy Agency (IAEA) in the year 2022[1]. IAEA distributed one clay and one plant sample to Member state laboratories worldwide to more than 80 to maintain their capabilities and services by producing reference materials and developing standardized analytical methods. The laboratories requested to submit the measurand mass faction in the environmental samples without the restriction of number of elements by nuclear and related analytical methods. We participated in this proficiency test to compare our laboratory results with other dynamic competitive INAA laboratories in the world.

2. Methods and Results

2.1 Experimental details

A wide range of elements (trace, minor, and major) were analysed in the siliceous clay and sterilized plant-derived cellulose powder samples. The dry mass of samples was determined using the oven drying method for clay sample (97.78%) and the desiccator method with desiccant $Mg(ClO_4)_2$ for plant sample (93.07%). 200 mg of sample wrapped with cellulose filter paper (Whatman filter paper No. 542) and prepared 13 mm diameter and 1~2 mm thick pellet. The National Institute of Standards and Technology (NIST) standard reference material (SRM) 2710a Montana soil I is used as a comparator. The samples rabbits were irradiated for 30 min (for medium-lived radionuclides) and 2 h (for long-lived radionuclides) at high thermal neutron position, PTS-2 of HANARO research reactor, Daejeon (ϕ = 2.3 × 10^{13} cm^{-2} s^{-1}, f = 1268±87). After an adequate cooling period, medium and long-lived radionuclides assay was carried out using an HPGe detector in conjunction with an auto-sample changer. Thirty elements of medium and long-lived radionuclide elements in clay sample, Ag, As, Ba, Br, Ce, Co, Cr, Cs, Eu, Fe, Hf, Hg, K, La, Lu, Na, Nd, Rb, Sb, Sc, Se, Sm, Ta, Tb, Th, U, W, Yb, Zn, Zr, and six elements, K, Na, Zn, Br, Rb, Sb, were analysed in plant sample through comparator INAA methodology. Sample preparation procedures and calculation procedures were published in previous publications [3].

2.2 PT performance indicators

All reported mass fractions of measurands were compared with the assigned or consensus values by using Z-score and R-score indicators for the labs.

Z- and R-scores were calculated using the following equations [1],

$$z_i = \frac{(x_i - x_{pt})}{\sigma_{pt}}$$

$$R_i = \frac{x_i}{x_{pt}}$$

x_i: reported mass fraction of the measurand
x_{pt}: Certified / assigned values by PT
σ_{pt}: uncertainty defined given by PT

The conventional interpretation of the Z-score is as follows as per the ISO/IEC 17043:2010,

|Z|≤2 the result is considered acceptable
2<|Z|<3 the result is considered and warning signal
|Z|≥3 the result is considered unacceptable

2.3 PT results interpretation

Our laboratory-reported values for the clay sample are presented in Table 1 along with the certified or assigned values provided by PT organizer, and lab scores. The certified property value (bold) from external provider or the consensus values (non-bold) of the submitted results. The bar chart distribution of results reported by worldwide laboratories of the specific measurand, and for Br is shown in Fig.1. The compiled Z-scores of measurands submitted from KAERI is shown in Fig.2. In the clay sample, 30 measurands were determined using INAA method. Among these measurands, 29 measurands were considered for evaluation and only Se was not considered for evaluation due to limited laboratories reported the measurand. All reported measurand values fall in the accepted range |Z|≤2 except two measurands Hg and Zr (|Z|≥3). The reported values are well in agreement with assigned values, and R-score also within the range of ±10%. These results showed that the laboratory-reported measurands have obtained good scores [1].

Table 1 Reported results (mg·kg^{-1}) for clay sample and performance score in IAEA PT excercise

Analyte	Reported	Assigned	Z-score	R-score
Ag	2.298±0.205	2.360±0.446	-0.42	0.94
As	38.204±1.645	38.300±2.565	-0.03	1.00
Ba	871.77±46.545	900.0±46.8	-0.55	0.97
Br	11.670±0.494	12.7±0.9	-0.74	0.92
Ce	61.387±1.615	59.2±6.08	0.43	1.04
Co	19.306±0.939	18.3±2.05	0.53	1.05
Cr	262.566±9.928	255±28.9	0.43	1.03
Cs	9.444±0.414	9.64±1.169	-0.18	0.98
Eu	1.077±0.043	1060±90	0.10	1.02
Fe	34410±1360	3420±1170	0.18	1.01
Hf	6.721±0.425	6.74±0.6	-0.03	1.00
Hg	5.494±0.203	2.91±0.251	6.52	1.89
K	19360±1170	18300±620	1.59	1.06
La	30.374±1.120	30.2±2.34	0.06	1.01
Lu	0.358±0.038	359±40	-0.02	1.00
Na	4860±250	4840±350	0.09	1.00
Nd	26.406±2.895	26.2±2.71	0.08	1.01
Rb	97.665±3.750	92.4±3.22	0.70	1.06
Sb	4.898±0.259	4.31±0.52	1.06	1.14
Sc	8.959±0.284	9.92±1.128	-0.86	0.90
Se	1.326±0.123	1.8±0.8	-	-
Sm	4.900±0.127	4.91±0.4	-0.02	1.00
Ta	0.854±0.073	900±120	-0.28	0.95
Tb	0.654±0.037	677±60	-0.19	0.97
Th	10.080±0.284	9.15±0.911	0.89	1.10
U	2.334±0.232	2.53±0.357	-0.84	0.91
W	6.902±0.642	7.10±1.4	-0.21	0.97
Yb	2.540±0.144	2.30±0.2	0.73	1.10
Zn	900.704±23.8	877±36.7	0.47	1.03
Zr	171.81±11.57	242±10.3	-4.41	0.71

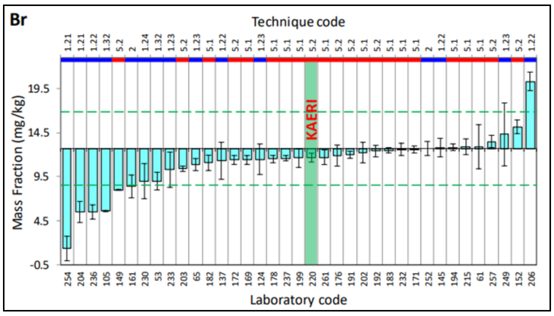

Fig. 1 Bar chart distribution of results reported by laboratories of Br in clay sample

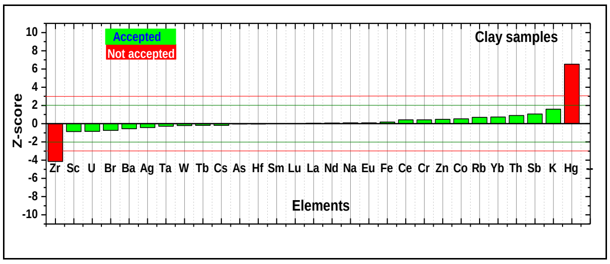

Fig. 2 Z-score values of KAERI INAA laboratory reported values in clay sample

In the plant sample, six measurands (Br, K, Na, Rb, Sb, and Zn) were determined using the INAA method. Among these measurands, three measurands were considered for evaluation, and Br, Na, and Sb were not considered for evaluation due to limited laboratories reported or variation of reported values is more than 10%. The bar chart distribution of results reported by laboratories Zn in plant sample is shown in Fig.3. The accepted for evaluation measurands values fell in the accepted range |Z|≤2. These results also showed that the laboratory-reported measurands have good scores [1].

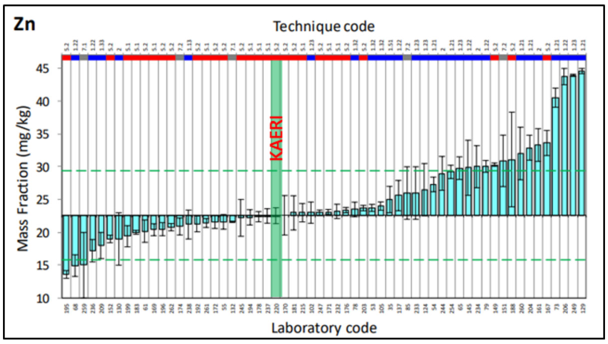

Fig. 3 Bar chart distribution of results reported by laboratories of Zn in plant sample

3. Conclusions

We have reported thirty elements in clay samples and six elements in plant samples to an inter-laboratory comparison study conducted by IAEA. Most of our results fell in the middle of the comparison chat and good agreement with assigned values and other laboratories. Overall, the performance score of the KAERI laboratory is good. These results are important to confirmation for the accurate and reliable analytical results produced by the INAA method using HANARO reactor. Based on these results, we are planning to renewal the KOLAS (Korea Laboratory Accreditation Scheme) accreditation to our laboratory for the specific matrix of samples.

REFERENCES

[1]. IAEA report on PTNATIAEA20:Worldwide Open Proficiency Test for Nuclear and Related Analytical Techniques Laboratories, 23 December 2022.

[2]. R.R. Greenberg, et. al., Neutron activation analysis: A primary method of measurement. Spectrochim. Acta B At. Spectrosc. 2011, 66, 193–241.

[3]. H. Cho, et. al., Application of the INAA methods for KRISS infant formula CRM analysis: standardization of INAA at KRISS. J. Radioanal. Nucl. Chem. 2019, 322, 1537–1547.