The Nucleus, **42** (3-4) 2005 : 153-158

The Nucleus
A Quarterly Scientific Journal of Pakistan Atomic Energy Commission
NCLEAM, ISSN 0029-5698

PERFORMANCE INDICATORS IN PROFICIENCY TEST EXERCISES

S. WAHEED*, A. RAHMAN, N. SIDDIQUE, J.H. ZAIDI and S. AHMAD

Nuclear Chemistry Division, Pakistan Institute of Nuclear Science and Technology (PINSTECH), P.O. Nilore, Islamabad, Pakistan

(Received June 21, 2006 and accepted in revised form August 4, 2006)

Normalized performance for individual participating laboratories in a proficiency test exercise for the determination of radionuclides in mushroom reference material were assigned through three quality indicators. Relative bias, z- scores and u-test scores were calculated for the data on ^{134}Cs, ^{137}Cs and ^{40}K submitted by laboratories representing six different countries. Data received for these radionuclides were statistically evaluated to obtain consensus mean values of 4.4 Bq/kg, 2899 Bq/kg and 1136 Bq/kg for ^{134}Cs, ^{137}Cs and ^{40}K respectively at a confidence intervals (at a significance level of 0.05). The target values for the standard deviation (σ) calculated for this exercise are 18.9%, 6.9%, 9.9% for ^{134}Cs, ^{137}Cs and ^{40}K, respectively, and have been assigned on the basis of the reproducibility standard deviation. Due to the small data sets for each radionuclide the limiting value for the u-test parameter was taken as 1.95 to determine if a result passes the test.

Keywords : Mushrooms, Proficiency test, Radionuclides, Reference materials, U-test, Z- score

1. Introduction

Stringent guidelines for a general quality system have been formulated by international bodies such as A Focus for Analytical Chemistry in Europe (EURACHEM), International Union of Pure and Applied Chemistry (IUPAC) and The International Organization of Standardization (ISO) etc. to be applied in analytical laboratories to trace and document their results in such a way that compatibility between laboratories can be obtained [1-2]. These guidelines recommend a regular, independent assessment of the technical performance of a laboratory to assure the validity of analytical measurements as a part of an overall quality management strategy. This can also reveal competence of the laboratory and establish credibility to national and international customers. For this reason there is a permanent requirement for such laboratories to test their performance by participation in proficiency tests (PTs) and inter-laboratory comparison exercises (ICEs) [3].

International Atomic Energy Agency (IAEA) has for the past three decades been organizing different PTs and ICEs through its analytical quality control services (AQCS) for its member states to evaluate the trends of their analytical performance in accordance with ISO, 1997 [4,5]. IAEA designed an interregional project INT/1/054, entitled "Preparation of Reference Materials and Organization of Proficiency Test Rounds" with an endeavor to prepare the participating nations for the production of reference materials (RMs) and future organization of PTs in their respective countries. This exercise also served to estimate the proficiency of the analytical laboratories of the countries participating in this project for the determination of different constituents such as different radionuclides and heavy metals. Edible mushrooms were selected as a suitable material for this purpose. They not only accumulate heavy and alkaline metals but also contain a significant amount of ^{137}Cs. Six countries namely Brazil, Hungary, Korea, Pakistan, Poland and Syria participated and submitted data in this proficiency test exercise for the determination of radionuclides in edible mushroom material.

The neutron activation analysis (NAA) laboratory at Pakistan Institute of Nuclear Science and Technology (PINSTECH) represented Pakistan in this project. This laboratory is the first PAEC laboratory and one of the few laboratories in Pakistan to obtain formal national accreditation under ISO/IEC-17025 by the Pakistan National Accreditation Council (PNAC). The NAA laboratory has been a regular participant in IAEA analytical quality control exercises to maintain confidence in its analytical capabilities for the past two decades

* Corresponding author : skhalid161@yahoo.com

Table 1. Summary of ^{134}Cs, ^{137}Cs and ^{40}K results in mushroom reference material.

Radionuclide	^{134}Cs	^{137}Cs	^{40}K
Overall mean (Bq/kg)	4.38	2898.9	1135.7
Abs. std. dev. (Bq/kg)	0.83	198.7	112.6
Rel. std. dev (%)	18.9	6.9	9.9
Standard error (abs)	0.50	81.1	46
Standard error (%)	10.9	2.8	4.0
Median (Bq/kg)	4.14	2885	1135
Range of values (Bq/kg)	3.7 - 5.3	2680 - 3192	1001 - 1319
Number of laboratories	3	6	6
No. of results averaged	7	22	22

[6-9] and was hence assigned the task of compiling Proficiency test report on radionuclides determination in the RM for the different participating countries by IAEA. As recommended in ISO/IEC Guide 43-1, the commonly used performance indicators for evaluation of quantitative results in PTs including relative bias, z-scores and u-test scores were applied. This paper presents the statistical evaluation of the results submitted by different countries.

2. Materials and Methods

Wild mushrooms, Xerocomus Badius, family Boletaceae were selected for this study. The mushrooms were collected from Poland where they are easily available in the forests. The mushrooms were cut into small pieces and air dried in a dryer at a temperature of 25-60^{o}C. The mushroom material was then sent to the Institute for Reference Materials and Measurements (IRMM) Laboratory, Geel, Belgium for final preparation. Further processing of this material was performed at this institute by the participants of the project under the guidance of IAEA and IRMM experts. The material was further milled using ZrO_2 planetary ball mill and sieved through 125 µm sieves and homogenized by mixing. The homogenized samples were then bottled and distributed to participating laboratories.

All participants were supplied with bottles containing 20 g samples and were asked to perform analysis of the samples in selected laboratories in their countries. A request was made to the participants to make at least three, but preferably six independent determinations and to report mean values, uncertainties and limit of detection for each radionuclide. Each laboratory was assigned a code number thus securing anonymity. The moisture content of the material was determined by drying to a constant weight at 50^{o}C. The participants were requested to determine in a separate subsample (not used for analysis) by drying to a constant weight at 50^{o}C (usually at least for 24 hours) and report all the results on dry weight basis. The results from 6 different countries were received. Three laboratories determined ^{134}Cs, all 6 laboratories determined ^{137}Cs and ^{40}K.

3. Evaluation of the Results

Results for three radionuclides, i.e. ^{134}Cs, ^{137}Cs and ^{40}K, in the mushroom reference material are presented in Table 1. These results were reported by three or more laboratories hence could be subjected to statistical evaluation. The details of the individual laboratory mean values, reported uncertainties (absolute and relative), sample mass and moisture content are presented in Tables 2 – 4 for these three radionuclides.

Computer based program, Histo Version 2.1 developed by IAEA, was applied to the original data for ^{134}Cs, ^{137}Cs and ^{40}K. The four outlier tests i.e. Dixon, Grubbs, Skewness and Kurtosis were applied to these data sets. All values for these three radionuclides were accepted by the software. Consensus (overall) mean values, absolute standard deviation, relative standard deviation, standard error, median and range of values for these three radionuclides in the IAEA mushroom reference material are reported in Table 5a, 5b and 5c. The results were further evaluated for assessing the difference between the consensus

Table 2. ^{134}Cs results of participant laboratories in mushroom reference material.

Lab. code	Mean value (Bq/kg)	Uncertainty (Bq/kg)	Relative Uncertainty (%)	Mass (g)	Dry/wet ratio
C1	3.70	0.90	24.32	NR	NR
C2	-	-	-	-	-
C3	-	-	-	-	-
C4	4.14	0.93	22.37	3.75	0.934
C5	5.30	2.10	39.62	9.63	0.930
C6	-	-	-	-	-

NR= Not reported

Table 3. ^{137}Cs results of individual laboratory in mushroom reference material.

Lab. code	Mean value (Bq/kg)	Uncertainty (Bq/kg)	Relative Uncertainty (%)	Mass (g)	Dry/wet ratio
C1	2680.00	170.00	6.34	NR	NR
C2	2710.00	140.00	5.17	NR	NR
C3	3192.00	27.00	0.85	37.50	0.929
C4	3039.46	30.29	1.00	3.75	0.934
C5	2948.67	98.33	3.33	9.80	0.932
C6	2823.21	36.56	1.29	2.20	NR

NR= Not reported

Table 4. ^{40}K results of individual laboratory in mushroom reference material.

Lab. code	Mean value (Bq/kg)	Uncertainty (Bq/kg)	Relative Uncertainty (%)	Mass (g)	Dry/wet ratio
C1	1130.0	80.0	7.1	NR	NR
C2	1001.0	50.0	5.0	NR	NR
C3	1140.0	22.0	1.9	37.50	0.929
C4	1319.3	53.4	4.0	3.75	0.934
C5	1183.7	95.5	8.1	9.80	0.932
C6	1040.0	136.0	13.1	NR	NR

NR= Not reported

value and the reported value using the following parameters:

3.1. Relative bias (%)

The relative bias between the analyst's value and the consensus mean expressed as a percentage:

$$\text{Relative bias} = \frac{\text{Value}_{\text{analyst}} - \text{Value}_{\text{mean}}}{\text{Value}_{\text{mean}}} \times 100\%$$

3.2. Z- scores

This type of score represents a simple method of giving each participant a normalized performance score for bias. This method of

Table 5a. Comparison of ^{134}Cs results against the consensus values in mushroom reference material.

Lab. Code	Mean (Bq/kg)	Uncertainty (Bq/kg)	Rel. uncertainty (%)	Analyst/ consensus ratio	Rel. bias (%)	z-score	Status	u-score	Status
C1	3.70	0.90	24.32	0.84	-15.5	-0.8	Pass	0.6	Pass
C4	4.14	0.93	22.37	0.95	-5.5	-0.3	Pass	0.2	Pass
C5	5.30	2.10	39.62	1.21	21.0	1.1	Pass	0.4	Pass

Table 5b. Comparison of ^{137}Cs results against the consensus values in mushroom reference material.

Lab. Code	Mean (Bq/kg)	Uncertainty (Bq/kg)	Rel. uncertainty (%)	Analyst/ consensus ratio	Rel. bias (%)	z-score	Status	u-score	Status
C1	2680.0	170.0	6.3	0.92	-7.6	-1.1	Pass	0.8	Pass
C2	2710.0	140.0	5.2	0.93	-6.5	-1.0	Pass	0.8	Pass
C3	3192.0	27.0	0.8	1.10	10.1	1.5	Pass	1.5	Fail
C4	3039.5	30.3	1.0	1.05	4.8	0.7	Pas	0.7	Pass
C5	2948.7	98.3	3.3	1.02	1.7	0.3	Pass	0.2	Pass
C6	2823.2	36.5	1.3	0.97	-2.6	-0.4	Pass	0.4	Pass

Table 5c. Comparison of ^{40}K results against the consensus values in mushroom reference material.

Lab. Code	Mean (Bq/kg)	Uncertainty (Bq/kg)	Rel. uncertainty (%)	Analyst/consensus ratio	Rel. bias(%)	z-score	Status	u-score	Status
C1	1130.0	80.0	7.1	1.00	-0.5	-0.1	Pass	0.0	Pass
C2	1001.0	50.0	5.0	0.88	-11.9	-1.2	Pass	1.1	Pass
C3	1140.0	22.0	1.9	1.00	0.4	0.0	Pass	0.0	Pass
C4	1319.3	53.4	4.0	1.16	16.2	1.6	Pass	1.5	Fail
C5	1183.7	95.5	8.1	1.04	4.2	0.4	Pass	0.3	Pass
C6	1040.0	136.0	13.1	0.92	-8.4	-0.8	Pass	0.5	Pass

assessing laboratories has been accepted as a standard for ISO/IUPAC [3, 10]. The z-score value was calculated according to the following equation:

$$Z_{score} = \frac{Value_{analyst} - Value_{mean}}{\sigma}$$

- The target values for the standard deviation (σ) have been assigned on the basis of the reproducibility standard deviation (the standard deviation of the consensus mean after outlier rejection which expresses inter-laboratory precision) calculated for this exercise are 18.9%, 6.9%, 9.9% for ^{134}Cs, ^{137}Cs and ^{40}K, respectively.
- Performance was considered to be acceptable if this difference was less than or equal to two ($|Z| \leq 2$);
- The results were of questionable quality when: $2 < |Z| < 2$
- The measurement was regarded as out of acceptable range when: $|Z| \geq 3$.

3.3. U-test

The value of u-test score was calculated according to the following equation:

$$u_{test} = \frac{\left|Value_{mean} - Value_{analyst}\right|}{\sqrt{Unc^2_{mean} + Unc^2_{analyst}}}$$

Here U_{nc} is the uncertainty. The calculated u-test value is compared with the critical values listed in the t-statistic tables to determine if the reported result differs significantly from the expected value at a given level of probability [11]. It should be noted that the choice of the significance level is subjective. For this proficiency test the limiting value for the u-test parameter is selected to be 1.95 to determine if a result passes the test (u < 1.95). This fairly large limit was applied keeping in view the small number of participating laboratories reporting small number of values.

4. Results and Conclusions

The participating countries were requested to report the results of different radionuclides together with the corresponding combined standard uncertainties. As the material used was being analyzed for the first time no certified or reference property values were available and the target values were derived from the consensus means obtained from this proficiency test exercise. Only three radionuclides were reported by more than one laboratory i.e. ^{134}Cs, ^{1374}Cs and ^{40}K, therefore these were assigned property values. The results are organized according to the laboratory code in ascending order. The error bars used in the figure represent the laboratory ratio (±) combined standard uncertainty for the ratio. The horizontal dashed lines represent (±) two standard deviation of the overall mean of these ratios.

Only three laboratories reported results of analysis for ^{134}Cs. All seven values provided were accepted on the basis of outlier tests, resulting in a relatively large uncertainty. As a consequence of this large uncertainty all laboratory mean results passed the z-score, u-test score criteria (Tables 5.a. to 5.c).

All six participating laboratories provided results for ^{137}Cs and 22 values were available. Concentration of this radionuclide was the highest and overall standard deviation of laboratory means was the lowest amongst the three selected radionuclides, reflecting best analytical results for this radionuclide. Using 95% confidence criteria all results passed.

A similar number of results were received for ^{40}K from all six participating laboratories. The uncertainties were slightly higher as compared to ^{137}Cs as was the range of values. However, all reported values were acceptable on the basis of outlier tests.

The final summary of consensus means and associated confidence intervals (at significance level 0.05) for ^{134}Cs, ^{137}Cs and ^{40}K are presented in Table 6. Recommended values could not be formulated because of the very limited data.

Table 6: Summary of means and confidence intervals for radionuclides in mushroom reference material.

Radionuclide	Mean Value (Bq/kg)	Confidence Interval (Bq/kg)
^{134}Cs	4.4	3.4-5.3
^{137}Cs	2899	2740-3058
^{40}K	1136	1046-1226

* Confidence intervals are for significance level of 0.05

Acknowledgement

The authors are thankful to Dr. Matthias Rossbach and Dr. Zbigniew Radecki Technical Coordinators of IAEA project INT/1/054 entitled Preparation of reference materials and organization of proficiency test rounds, for giving the opportunity to compile the international data.

Finally all the laboratories who participated in this exercise are also acknowledged.

References

[1] M. Thompson and R. Wood, Harmonized Guidelines for Internal Quality Control in Analytical Chemistry Laboratories, IUPAC Technical Report, Oxford, UK (1995).

[2] P. Bode, J. Radioanal. Nucl. Chem., **215** (1997) 51.

[3] ISO/IEC, Proficiency testing by interlaboratory comparisons, Part 1, ISO Guide 43-1, 1997, International Standard Organization: Geneva.

[4] M. Coquery, F. P. Carvalho, S. Azemard and M. Horvat, The Sci. of the Total Environ., **237/23** (1999) 501.

[5] P. P. Povinec, Future challenges of IAEA's AQCS programme, IAEA-MEL Report 5/96, Monaco, (1996).

[6] A. Mannan, S. Waheed, A. Rahman, S. Ahmad and I. H. Qureshi, Geostandards Newsletter; **17**, No. 1 (1993) 223.

[7] S. Waheed, M. Waseem, A. Rahman, and S. Ahmad, Geostandards Newsletter, **25** (2001) 137.

[8] M. Waseem, A. Rahman, J. H. Zaidi, S. Waheed, and S. Ahmad, J. Radioanal. Nucl. Chem., **248** (2001) 205.

[9] S. Waheed, A. Rahman, M. Daud, J. H. Zaidi and S. Ahmad, Radiochim. Acta,, **92** (2004) 939.

[10] M. Thompson and R. Wood, The international harmonized protocols for the proficiency testing of (chemical) analytical laboratory studies, IUPAC/ISO/AOAC, J. Pure Appl. Chem., **65** (1993) 2123.

[11] C.J. Brookes, I. G. Betteley and S. M. Loxton, Fundamentals of Mathematics and Statistics, Wiley USA (1979).