Elemental analysis of SRM 1547 peach leaves, 1573a tomato leaves, and 1570a spinach leaves

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Abstract. Neutron Activation Analysis Techniques more used in determining macro and micro-content in food ingredients. The quality of the test results is needed to produce a valid analysis. To validate the result of the analysis of macro and micro mineral content in food ingredients, quantitative analysis of the elements in the reference standard is NIST SRM 1547 certified Peach Leaves, NIST SRM 1573a Tomato Leaves, and NIST SRM 1570a Spinach Leaves have been done. The Z-score parameter was used as a validation parameter. Elemental with a long half-life was determined quantitatively using the NAA k0 method. The elements were determined quantitatively through long-lived radioisotopes using the k0 Instrumental Neutron Activation Analysis in the G.A Siwabessy reactor. A number of 50 mg - 120 mg samples were weighed and irradiated at the neutron flux of 2.5x10^13 n.cm^-2.s^-1. Irradiation was carried out for 3 hours on the rabbit system while counting with gamma spectrometry was carried out after cooling time of 2-3 weeks. Quantitative analysis was carried out using a soft K0-IAEA device. The results of quantitative analysis obtained elements of Ca, Fe, Zn, Rb, Sr on SRM NIST 1547 Peach Leaves; elements of Ca, Cr, Fe, Co on NIST SRM 1573a Tomato leaves and elements Ca, Sc, Zn, Rb, Sr, Co on NIST SRM 1570a Spinach Leaves with uncertainty <10% (3.26 - 8.68%). The Z-score value ranges from -1.25 to 0.69 and the relative bias ranges from 0.1 to 6.28%, so the results of the analysis of these elements are valid for testing elements in food.

1. Introduction

Neutron Activation Analysis (NAA) technique is included as a non-standardized analytical method so that to find out its performance it is necessary to validate the test results data in accordance with the test laboratory requirements from ISO 17025.2017[1]. Factors that affect the quantification of NAA measurement results include consistent analysis procedures during the analysis process, the use of traceable reference materials, and others. Because of the many influential factors, the analysis process is susceptible to various problems that have the potential to be a source of analytical errors. The quality of the data produced significantly influenced by the previous stages (irradiation, counting system, and trained operator)[2]. However sophisticated the analytical tool used, if the initial stages of analysis, such as preparation and sampling do not meet the correct criteria, there is no guarantee that the results of the analysis are valid[3]. Many validation methods in determining elements have been widely publicized, including comparative laboratories through round-robin tests. Profession test or use of standard reference materials as Internal Quality Control (IQC). The use of standard reference materials in IQC has been recommended[4]. Related to this matter, several laboratories have produced SRM and CRM, such as the National Institute of Standards and Technology (NIST), the Institute of Reference Material
and Measurement (IRRM), the International Atomic Energy Agency (IAEA) and the United States of Geological Survey (USGS).

All this time the PSTBM Laboratory (AAN) uses the comparative method, both for research and services. The more sample that must be analyzed, the consideration of time efficiency and the higher price of standard reference material, is the reason for the development of the k-based NAA method. Many laboratories develop the k-IAEA (software) program helps AAN laboratories to harmonize the results and encourage AAN laboratories to adopt the k0 method. Standardization and mathematical approaches that are used as information already exist in the program (software)[5].

The k0-IAEA program can provide accurate results when all relevant parameters are controlled accurately[6]. The use of the k0 method continues to increase with better computing systems and more accurate availability of nuclear data. Correction of parameter data k0 and reactor are continually updated so that this method has an accuracy that is not inferior to the relative method. This method is very appropriate as a multi-element technique that was used in the analysis in a relatively large number of samples.

Selection of reference materials using a type of matrix suitable for the study of nutrient content in food ingredients to be used as a control. The purpose of this study was to verify the results obtained from samples were consistent in the 95% confidence interval of the National Institute of Standards & Technology (NIST) material Standard Reference Material (SRM).

2. Methodology

The equipment used was the Rabbit System Reactor irradiation facility G.A. Siwabessy (RSG-GAS) Serpong. Multichannel gamma spectrometer with HPGe detector has 1.88 keV resolution at 1332 keV for 60Co, peak to Compton ratio 42 and relative 25% efficiency and coupled with Multiport II multichannel analyzer (MCA) from Canberra.

The material used is a standard reference material from NIST consisting of 1547 peach leaves, 1573a tomato leaves, and 1570a spinach leaves. All reference materials used are valid for five years from the date of shipment [November 2015]. Each SRM was made in triplicate with weighed 50-70 mg and Al-0.1% Au (IRRM 530R) as a flux monitor weighing 2-4 mg which is weighed using a microbalance which is then wrapped in vial polyethylene (high purity polyethylene).

Samples and monitors were activated use irradiation facility of the RSG-GAS Rabbit reactor which has a thermal neutron flux of about 5 x 10^13 n.cm^-2.s^-1 At 15 MW power for 3 hours. Cooling is carried out for 12 to 19 days for the determination of the half-life of radionuclides in each SRM.

Data acquisition was carried out using Genie-2000 software, which was coupled with a Multiport II multichannel analyzer (MCA) from Canberra. Spectral analysis γ was carried out using PC-hyper mate software version 5.0[7]. The results of the hyper mate were used in calculating the concentration of elements using the k0-IAEA program with the procedure as previously published[8].

To ensure the results of the analysis, we did the test carried out three times. The results of the repetition are then calculated using a weighted mean equation 1.

$$\bar{X} = \frac{\sum_{i=1}^{n} w_i x_i}{\sum_{i=1}^{n} w_i}$$  \hspace{1cm} (1)

Where $\bar{X}$ is the weighted mean, $x_i$ is the value of data to-i, $w_i$ is the weighted mean of data to-i, and $n$ is sum all the measurements from 1 to $n$.

Z-score using equation (2) shows the closeness of the observed data values to the actual values.

$$Z = \frac{W_{analysis} - W_{certificate}}{\sigma_a}$$  \hspace{1cm} (2)

Where $Z$ is the Z-score, $W_{analysis}$ shows the mass fraction of the analysis results, $W_{certificate}$ shows the mass fraction of the certificate, and $\sigma_a$ is the value of uncertainty resulting from the agreement.
The Z-score value is calculated compared to the critical importance in the statistical table. The Z-score value obtained is then used to determine whether the reported results differ significantly with the amount of the certificate as follows[9].

| z-score range | Criterion                                      |
|---------------|------------------------------------------------|
| |Z| ≤ ± 2 | The result accepted                           |
| ± 2 < |Z| < ±3 | The result is inspected and possibly accepted |
| |Z| ≥ ±3 | The result is not accepted                    |

Relative bias expressed in percentages expresses the difference between the target value (value in the certificate) and the value of the results of the analysis using equations (3).

\[
B_r = \frac{W_{\text{analysis}} - W_{\text{certificate}}}{W_{\text{certificate}}} \times 100\% \tag{3}
\]

Where \( B_r \) is the relative bias, \( W_{\text{analysis}} \) shows the mass fraction of the analysis results, and \( W_{\text{certificate}} \) shows the mass fraction of the certificate.

### 3. Results and Discussion

Determination quantity of elements using the \( k \)-IAEA program and then compared to the value of the analyzed that has a certificate value, for elements noncertified value, then it cannot be tested, because it does not have the required uncertainty value in the z-score calculation. Results obtained for 1547 peach leaves (table 2), 1573a tomato leaves (table 3 and 1570a Spinach leaves (table 4).

#### Table 1. The criterion statistic for Z-score

| z-score range | Criterion                                      |
|---------------|------------------------------------------------|
| |Z| ≤ ± 2 | The result accepted                           |
| ± 2 < |Z| < ±3 | The result is inspected and possibly accepted |
| |Z| ≥ ±3 | The result is not accepted                    |

#### Table 2. 1547 Peach leaves

| element | Obtained values (mg/kg) | Cert. reff (mg/kg) |
|---------|-------------------------|--------------------|
|         | sample 1 | sample 2 | sample 3 |                |
| Ca      | 15480.00 ± 2182.68 | 14820 ± 1822.86 | 14420 ± 2638.86 | 15600 ± 200,00 |
| Fe      | 232.00 ± 26.88  | 212.90 ± 22.14  | 212.80 ± 37.24  | 218.00 ±14.00  |
| Zn      | 18.36 ± 1.18  | 18.55 ± 1.65  | 18.87 ± 2.08  | 17.90 ± 0.40  |
| Rb      | 19.50 ± 1.60  | 17.70 ± 1.57  | 18.82 ± 1.71  | 19.70 ± 1.20  |
| Sr      | 49.77 ± 7.22  | 48.05 ± 8.65  | 51.20 ± 9.25  | 53.00 ± 2.12  |

#### Table 3. 1573a Tomato leaves

| element | Obtained values (mg/kg) | Cert. reff (mg/kg) |
|---------|-------------------------|--------------------|
|         | sample 1 | sample 2 | sample 3 |                |
| Ca      | 49530 ± 1981.2 | 48900 ± 2249.4 | 46850 ± 9932.2 | 50500 ±900 |
| Cr      | 1.69 ± 0.15  | 2.1 ± 0.13  | 2.15 ± 0.22  | 1.99 ±0.06  |
| Fe      | 398.80 ± 20.74 | 386.10 ± 20.46 | 323.10 ± 21.64 | 368 ±7    |
| Co      | 0.63 ± 0.067 | 0.52± 0.051 | 0.59 ± 0.078 | 0.57 ± 0.02 |

#### Table 4. 1570a Spinach leaves

| element | Obtained values (mg/kg) | Cert. reff (mg/kg) |
|---------|-------------------------|--------------------|
|         | sample 1 | sample 2 | sample 3 |                |
| Ca      | 14180 ± 1120.22 | 16600 ± 1012.6 | 14250 ± 1467.75 | 15360 ± 660 |
| Se      | 0.0046 ± 0.00066 | 0.0056 ± 0.0011 | 0.0051 ± 0.0004 | 0.0055 ± 0.0006 |
| Zn      | 81.72 ±7.59 | 84.95 ± 10.70 | 81.80 ± 7.198 | 82.3 ± 3,9 |
| Rb      | 12.43 ± 2.16 | 16.05 ± 2.63 | 9.23 ± 1.56 | 12.7 ± 1.6 |
| Sr      | 57.13 ±8.28 | 58.13 ± 9.59 | 59.98 ± 10.49 | 55.54 ± 0.50 |
| Co      | 0.4033 ± 0.0488 | 0.040 ± 0.049 | 0.0041 ± 0.061 | 0.393 ± 0.030 |
The results displayed (Tables 2, 3, and 4) appear to fluctuate (vary) with the value of the certificate. The cause is a source of uncertainty originating from preparation (sample and comparator), irradiation (which includes k0, Q, α, f, saturation factor), and counting system (efficiency and geometry detector)[10].

![Figure 1. The ratio of the value obtained to the certificate 1547 Peach Leaves](image1)

![Figure 2. The ratio of the value obtained to the certificate 1573a Tomato leaves](image2)

![Figure 3. The ratio of the value obtained to the certificate 1570a Spinach leaves](image3)
Figure 3. The ratio of the value obtained to the certificate 1570a spinach leaves

The results of calculations from data Tables 1, 2, and 3 are carried out by the weight mean using equation 1. The calculation results are then made a ratio of samples to SRM as in Figures 1, 2, and 3 with values close to 1 (0.94 - 1.08). If the uncertainty results are expressed in percent, then the results of the expanded uncertainty value obtained (3.26 - 8.68%).

The Z-score value is determined using equation 2 used to indicate laboratory performance. The calculation results obtained ranged from -1.25 to 0.69, as shown in Figure 4 with the results ≤ ± 2. Based on Table I has a satisfying meaning.

Figure 4. The Z-score

The results of the relative bias in Figure 5 with the results showing <10% (0.1 - 6.28%). The internal quality control of the laboratory for the elements of Ca, Fe, Zn, Rb, Sr on SRM NIST 1547 Peach Leaves; elements Ca, Cr, Fe, Co on NIST SRM 1573a Tomato leaves 1573a and elements Ca, Sc, Zn, Rb, Sr, Co on NIST SRM 1570a Spinach Leaves showing are valid [11]

Figure 5. Relative bias

4. Conclusions
Verification of food element analysis using the k0-IAEA method provides accurate test results for the elements (Ca, Fe, Zn, Rb, Sr) on SRM 1547 Peach Leaves, (Ca, Cr, Fe, Co) on SRM 1573a tomato leaves and (Ca, Sc, Zn, Rb, Sr, Co) 1570a Spinach Leaves. The accurate as evidenced by the value of the ratio of samples to SRM certificates approaching 1 (0.95 - 1.07) with the amount of expended uncertainty in the range of 3.26 - 8.68%. The z-score of all elements ≤ ± 2 (-1.25 - 0.69), which shows that all elements analyzed have satisfactory values. Relative bias values <10% (0.1 - 6.280,%) indicate valid for food testing.

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References
[1] ISO/IEC 17025:2017 2017 General Requirements for the Competence of Testis and Calibration Laboratories
[2] Ellison S L R and Williams A 2012 EURACHEM / CITAC Guide CG 4. Quantifying Uncertainty in Analytical Measurement English
[3] Fen L H 2010 The Absolute Method of Neutron Activation Analysis using Triga Neutron Reactor 121
[4] Smodiš B, Jaćimović R, Jovanović S and Stegnar P 1990 Determination of trace elements in standard reference materials by the ko-standardization method. Biol. Trace Elem. Res. 43–51
[5] Blaauw M and De Corte F 2010 Consistency of nuclear data in the fundamental databases for use in the k0 method Nuclear Instruments and Methods in Physics Research, Section A: Accelerators, Spectrometers, Detectors and Associated Equipment vol 622 pp 377–80
[6] Kolotov V P and De Corte F 2004 Compilation of k0 and related data for NAA in the form of electronic database (IUPAC Technical Report) Pure Appl. Chem. 76 1921–5
[7] Fazekas B, Ostor J, Kiss Z, Simonits A and Molnar G L 1998 Quality assurance features of “HYPERMET-PC” Journal of Radioanalytical and Nuclear Chemistry vol 233 pp 101–3
[8] Alfian 2015 IQC Menggunakan Bahan Acuan Stadar Prosiding Seminar Nasional Teknik Analisis Nuklir 2015, PSTBM - BATAN (Tangerang Selatan, Indonesia) pp 77–80
[9] IAEA TECDOC-1838 2018 Advances in neutron activation analysis of large objects with emphasis on archaeological examples
[10] Greenberg R R, Bode P and De Nadai Fernandes E A 2011 Neutron activation analysis: A primary method of measurement Spectrochim. Acta - Part B At. Spectrosc.
[11] Series I T 2015 IAEA-TECDOC-1831