Validation of $^{182}$Ta, $^{54}$Mn and $^{46}$Sc Radioactivity Measurements in Blue Topaz Using Gamma Spectrometric Analysis

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Abstract. Radioactivity is one of the most discussed topics surrounding blue topaz, which is commonly treated by neutron and/or electron irradiation from near-colorless initiating material. The detection of residual radioactivity after irradiation was usually done by the analytical method of gamma-ray spectroscopy. Therefore, using of validated methods is important for an analytical procedure to show performance and qualification of the method. This work describes the methods for validation of gamma spectrometric analytical procedure in the determination of some gamma emitters in blue topaz samples. Repeatability, reproducibility and minimum detectable activity were the main validation parameters.

1. Introduction
Blue topaz is one of the most popular colored gemstones in the jewelry market today, especially fashion-forward pieces and production lines. In nature, topaz is most common in transparent colorless and pale yellow colors. Blue topaz is achieved by a combination of irradiation and heat treatment. Sky Blue topaz (a lighter shade of blue) is the result of treatment of colorless topaz with either gamma rays from Cobalt 60 sources or electrons produced by electron accelerators, followed by a heat treatment. London Blue (a medium to dark grayish blue) and Swiss Blue (a deep blue) were produced by using the conjunction of neutron from a nuclear reactor, electron from a linear accelerator and heat treatment. In most cases electron accelerators at 10 MeV is used for treatment of topaz and these facilities cannot produce radioactivity in topaz. Also, if the electrons power is increased to 20 MeV, blue topaz can be activated for days or a few weeks. On the other hand, topaz treated with neutrons in a nuclear reactor turns radioactive from the nuclides of trace-element impurities [1, 2], such as Fe, Mn, Co, Zn, Sb, Ta, Cs, Sc, and Tb [3-5]. The decay rates of nuclides created by irradiation depend on the individual nuclides. The length of decay to be anywhere from hours to days to a few years. For this reason the health authorities have issued very strict rules for measuring of the activity in the topaz before they can be released from these irradiation facilities. The detection of residual radioactivity after irradiation was usually done by the analytical method of gamma-ray spectroscopy.

Quality control in gamma-ray spectrometry is an important process of operational techniques and activities that are used to fulfill the requirements of a quality system based on ISO/IEC 17025.
requires monitoring of the performance of the spectrometer, the analysis procedure and the consistency of the results. Therefore, using validated methods is important for an analytical procedure to show performance and qualification of the method. This work describes the methods for validation of gamma spectrometric analytical procedure in the determination of some gamma emitters in blue topaz samples. Repeatability, reproducibility and minimum detectable activity were the main validation parameters.

2. Material and method
Gamma spectrometry based on hyper-pure germanium detectors (HPGe) (Fig. 1) was used to measure the residual radioactivity of the irradiated blue topaz samples. The HPGe detector has a relative efficiency of 25% and full width at half maximum (FWHM) of 1.80 keV for $^{60}$Co gamma energy line at 1332 keV and operated with Canberra Genie 2000 software for gamma acquisition and analysis. The gamma ray spectrum represent the radioactivity of specific nuclides in irradiated topaz. The measurements were semi-quantitative, obtained for 3,600 seconds of counting time.

![Figure 1. HPGe detector system was installed since 2015 at the Gems Irradiation Center, Thailand Institute of Nuclear Technology (TINT).](image)

Four samples of cutting topaz (weighing ~10.0 g.) of pegmatite origin from Nigeria were studied. The samples were irradiated with $5.94 \times 10^{11}$ n cm$^{-2}$ s$^{-1}$ neutron flux in Thai Research Reactor 1/Modification 1 (TRR-1/M1) on March 28, 2014, and removed from the reactor on December 4, 2014. The decay time about 13 month till the experiment day.

Description of the analytical procedure and spectrometer calibration for the determination of the radioactivity is shown in Fig. 2.

![Figure 2. Analytical procedure for the determination of radioactivity of blue topaz samples.](image)

3. Results and discussion

3.1. Energy Calibration
The energy calibration of the HPGe detector system using the radioisotope calibration sources of $^{133}$Ba, $^{137}$Cs, $^{60}$Co, with characteristics described in their calibration certificates reference. The energy range of interest, 50 - 1332 keV, was used for this calibration. All the samples (including standards)
were counted directly in the same geometry and counting time. The centroid of photopeak of calibration sources were obtained the peak positions of gamma ray energy lines exhibited in Table 1.

### Table 1. Relation between peak position and energy lines of calibration source.

| Radioisotope | Gamma ray Energy [keV] | Channel number |
|--------------|------------------------|----------------|
| $^{133}$Ba   | 302.85                 | 905            |
|              | 356.02                 | 1064           |
| $^{137}$Cs   | 661.66                 | 1977           |
| $^{60}$Co    | 1173.24                | 3505           |
|              | 1332.50                | 3982           |

Taking into account above results, the calibration curve is described by the following second degree polynomial function:

$$\text{Energy} \ [\text{keV}] = a_0 + (a_1 \times \text{Channel}) + (a_2 \times \text{Channel}^2)$$

(1)

where $a_0 = -0.3987$, $a_1 = 0.3351$, $a_2 = -8 \times 10^{-8}$. These coefficients values are from the fitting curve represented in Fig. 3. The integral nonlinearity is $< 0.023\%$ in the interval of 50 - 1332 keV, the differential nonlinearity is $< \pm 0.1\%$.

![Figure 3. The energy calibration curve of the HPGe detector system.](image)

### 3.2. Efficiency Calibration

The source used for efficiency calibration was the europium mixed sources. The main gamma ray energy, the emission rate, the half-life and the certified activity, are listed in Table 2. The calibration sources were positioned at 2.54 cm distance from the end cap of the detector. All of the measured gamma spectra were analyzed using Genie 2000 program. After measurement of calibration sources, the experimental efficiencies in each dominant energy between range 100 and 1596 keV were calculated. The experimental efficiency at energy $E_{\gamma}$ for a given set of measuring conditions are:

$$E_{E_{\gamma}} = \frac{N_{E_{\gamma}}}{A_t I_{E_{\gamma}} t}$$

(2)

Where $N_{E_{\gamma}}$ is the net area in the region of interest of the full-energy peak corresponding to $E_{\gamma}$ energy photons emitted by a radionuclide with a known activity, $A_t$ and $I_{E_{\gamma}}$ is the probability of emitting a gamma
photon and \( t \) is the counting time. Efficiency curves were constructed from these calculated full-energy-peak efficiencies as shown in Fig. 4.

### Table 2. The characteristics of the europium mixed sources.

| Peak No. | Energy [keV] | Eu-152 (Photons/s) | Eu-154 (Photons/s) | Eu-155 (Photons/s) |
|----------|--------------|-------------------|-------------------|-------------------|
| 1        | 40.1 (SmKa)  | 5370              |                   |                   |
| 2        | 60.0         |                   | 105               |                   |
| 3        | 86.5         |                   | 2950              |                   |
| 4        | 105.3        |                   | 2060              |                   |
| 5        | 121.8 –doublet | 2640             | 3920              |                   |
|          | 123.1        |                   |                   |                   |
| 6        | 244.7        | 695               |                   |                   |
| 7        | 344.3        | 2460              |                   |                   |
| 8        | 591.7        |                   |                   |                   |
| 9        | 723.3        |                   | 447               |                   |
| 10       | 873.2        |                   | 1170              |                   |
| 11       | 1004.8       |                   | 1710              |                   |
| 12       | 1274.5       |                   | 3350              |                   |
| 13       | 1408.0       | 1930              |                   |                   |
| 14       | 1596.5       |                   | 180               |                   |

| Activity (Becquerels, Bq) | Eu-152 | Eu-154 | Eu-155 |
|---------------------------|--------|--------|--------|
| 9260                      | 9710   | 9520   |

| Activity (Microcuries)    | Eu-152 | Eu-154 | Eu-155 |
|---------------------------|--------|--------|--------|
| 0.250                     | 0.262  | 0.257  |

| Half-Life (Days)           | Eu-152 | Eu-154 | Eu-155 |
|---------------------------|--------|--------|--------|
| 4.96E+03                   | 3.14E+03 | 1.74E+03 |

| Decay Constant (Days\(^{-1}\)) | Eu-152 | Eu-154 | Eu-155 |
|--------------------------------|--------|--------|--------|
| 1.40E-04                      | 2.21E-04 | 3.98E-04 |

**Figure 4.** Efficiency calibration curve obtained for the reference geometry.

In Fig. 4, the efficiency curve was exhibited in log of efficiency vs. log of energy scales. In the 60-1408 keV range shows two regions of different behavior because distinct attenuation and absorption processes dominate. At below 100 keV energies the efficiency rises rapidly, but above a few hundred keV the efficiency decreases monotonically. For calculating activity of radioisotope \(^{182}\)Ta, \(^{46}\)Sc and \(^{54}\)Mn in irradiated topaz can use the efficiency curve above 100 keV, which showed the linear curve. Therefore, the efficiency fitting curve is described by a linear function as follow:
\[ y = b_1 x^2 + b_2 x + b_3 \]  
(3)

where \( y \) is logarithm of efficiency, \( x \) is the logarithm of energy and \( b_1, b_2 \) and \( b_3 \) are the fitting parameters, \( b_1 = -0.1698 \), \( b_2 = -0.0509 \), and \( b_3 = -0.2813 \), from the Fig. 4. The efficiency used for calculating activity of \(^{182}\text{Ta}, ^{46}\text{Sc} \) and \(^{54}\text{Mn} \) are mentioned in Table 3.

| Isotope | Energy [keV] | Branching ratio | Efficiency |
|---------|-------------|-----------------|------------|
| \(^{54}\text{Mn}\) | 834.89 | 0.9999 | 0.0132 |
| \(^{46}\text{Sc}\) | 889.28 | 0.9999 | 0.0124 |
| \(^{182}\text{Ta}\) | 1189.05 | 0.1623 | 0.0090 |
| \(^{137}\text{Cs}\) | 661.66 | 0.9436 | 0.0168 |
| \(^{60}\text{Co}\) | 1173.24 | 0.9985 | 0.0092 |

| Energy [keV] | Background count at ROI [s\(^{-1}\)] | MDA [Bq/gram] |
|-------------|---------------------------------------|---------------|
| \(^{54}\text{Mn}\) | 834.89 | 0 | 0.028 |
| \(^{46}\text{Sc}\) | 889.28 | 0 | 0.030 |
| \(^{182}\text{Ta}\) | 1189.05 | 0 | 0.256 |

3.3. Performance characteristics of test method

3.3.1. Activity Accuracy. The activity accuracy obtained after the efficiency calibration by setting the measuring conditions as used in measuring efficiency. The results are presented in the Table 3.

| Radionuclide | Point source code | Calculated actual activity [Bq] | Measured activity [Bq] | Accuracy [%] |
|--------------|-------------------|---------------------------------|------------------------|--------------|
| \(^{137}\text{Cs}\) | D-63-10 | 26229.60 | 27287.30 | 95.97 |
| \(^{60}\text{Co}\) | D-63-9 | 4821.80 | 4640.66 | 96.24 |

3.3.2. Minimum Detectable Activity (MDA). The calculation of Minimum Detectable Activity for \(^{182}\text{Ta}, ^{54}\text{Mn} \) and \(^{46}\text{Sc} \), at the 95% confidence level, are based on Currie’s derivation [6], with simplified formulation as follows:

\[
\text{MDA (Bq/unit wt)} = \frac{2.71+4.66(\sigma)}{T \cdot EFF \cdot I \cdot wt} \]

(4)

where \( \sigma \) is the standard deviation of the background collected during the counting time, \( (T, \text{ in sec}) \) over the energy range of interest (ROI), \( EFF \) is the efficiency at the energy of interest, \( I \) is the Branching Ratio and \( wt \) is sample weight. The MDA values of measuring nuclides are shown in Table 5.

| Radionuclide | Energy [keV] | Background count at ROI [s\(^{-1}\)] | MDA [Bq/gram] |
|--------------|-------------|-------------------------------------|---------------|
| \(^{54}\text{Mn}\) | 834.89 | 0 | 0.028 |
| \(^{46}\text{Sc}\) | 889.28 | 0 | 0.030 |
| \(^{182}\text{Ta}\) | 1189.05 | 0 | 0.256 |
3.3.3. The internal comparison. This part is most important for our measuring method. The internal comparison is a valuable part of validation, which having three participant and their various spectrometer systems for measuring one sample of blue topaz for this study. The results obtained by the three laboratories are presented in Table 6, indicating with high accuracy in comparable activity values. However, the activity values of $^{46}$Sc and $^{182}$Ta at R&D NAA Lab show lower than those at GIC labs. The difference in efficiency calibration method may take effect in high energy rang of gamma ray (more than 800 keV).

Table 6. The internal comparison results. (GIC stands for Gems Irradiation Center)

| Radionuclide | GIC Ongkharak* (Point source calibration) | GIC Bangkhen (Point source calibration) | R&D Group NAA Lab (ISOCS theoretical calibration) |
|--------------|------------------------------------------|-----------------------------------------|--------------------------------------------------|
| $^{54}$Mn    | 23.19                                    | 21.67                                   | 21.44                                            |
| $^{46}$Sc    | 449.78                                   | 460.10                                  | 371.38                                           |
| $^{182}$Ta   | 69.80                                    | 66.21                                   | 50.57                                            |

*GIC Ongkharak is the main lab, and the other two labs are used for comparison.

4. Conclusion

The validation of the results and of the calibration method was made in a series of measurements to check the values of the parameters declared in the HPGe detector technical documentation, using certified point sources and respecting the initial measuring conditions and also participating at three intercomparisons with the internal laboratory (GIC Lab. in Bangkhen branch and R&D Group NAA Lab). The results obtained by GIC Lab. in Ongkharak branch validate the measuring method, emphasizing the fact that our gamma spectrometric system with HPGe detector is properly calibrated in energy and efficiency, respecting the measurement geometry. The sample size of irradiated topaz used in this test is ~10 gram which may comparable to ~3.0 cm$^3$. Therefore, the difference in measurement geometry still have to find the solution. We will concentrate more in this issue.

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