Determination of $^{226}$Ra in TENORM Sample Considering Radon Leakage Correction

Soyeon Lim$^{1,2}$, Nur Syamsi Syam$^{1,3}$, Seongjin Maeng$^{1,4}$, Sang Hoon Lee$^{1,4}$

$^1$School of Architectural, Civil, Environmental, and Energy Engineering, Kyungpook National University, Daegu, Korea; $^2$Central Research Institute, Korea Hydro & Nuclear Power Co. Ltd., Daejeon, Korea; $^3$Directorate of Licensing for Nuclear Installations and Materials, Badan Pengawas Tenaga Nuklir (BAPETEN), Jakarta, Indonesia; $^4$Radiation Science Research Institute, Kyungpook National University, Daegu, Korea

Background: Phosphogypsum is material produced as a byproduct in fertilizer industry and is generally used for building materials. This material may contain enhanced radium-226 ($^{226}$Ra) activity concentration compared to its natural concentration that may lead to indoor radon accumulation. Therefore, an accurate measurement method is proposed in this study to determine $^{226}$Ra activity concentration in phosphogypsum sample, considering the potential radon leakage from the sample container.

Materials and Methods: The International Atomic Energy Agency (IAEA) phosphogypsum reference material was used as a sample in this study. High-purity germanium (HPGe) gamma spectrometry was used to measure the activity concentration of the $^{226}$Ra decay products, i.e., $^{214}$Bi and $^{214}$Pb. Marinelli beakers sealed with three different sealing methods were used as sample containers. Due to the potential leakage of radon from the Marinelli beaker (MB), correction to the activity concentration resulted in gamma spectrometry is needed. Therefore, the leaked fraction of radon escaped from the sample container was calculated and added to the gamma spectrometry measured values.

Results and Discussion: Total activity concentration of $^{226}$Ra was determined by summing up the activity concentration from gamma spectrometry measurement and calculated concentration from radon leakage correction method. The results obtained from $^{214}$Bi peak were 723.4 ± 4.0 Bq·kg$^{-1}$ in MB1 and 719.2 ± 3.5 Bq·kg$^{-1}$ in MB2 that showed about 5% discrepancy compared to the certified activity. Besides, results obtained from $^{214}$Pb peak were 741.9 ± 3.6 Bq·kg$^{-1}$ in MB1 and 740.1 ± 3.4 Bq·kg$^{-1}$ in MB2 that showed about 2% difference compared to the certified activity measurement of $^{226}$Ra concentration activity.

Conclusion: The results show that radon leakage correction was calculated with insignificant discrepancy to the certified values and provided improvement to the gamma spectrometry. Therefore, measuring $^{226}$Ra activity concentration in TENORM (technologically enhanced naturally occurring radioactive material) sample using radon leakage correction can be concluded as a convenient and accurate method that can be easily conducted with simple calculation.

Keywords: TENORM, $^{226}$Ra, Radon Leakage Correction, HPGe Gamma Spectrometry

Introduction

Naturally occurring radioactive material, generally known as NORM is material containing natural radionuclides such as uranium (U), thorium (Th), and actinium (Ac) series, and also $^{40}$K and few cosmogenic radionuclides. Radium-226 ($^{226}$Ra), one of the decay products of the uranium series, is an important radionuclide from radiological
risk point of view. This nuclide has half-life of 1,600 years and decays by emitting alpha and gamma radiation to produce radon-222 ($^{222}$Rn), the only gaseous radionuclide of the decay series as shown in Fig. 1 [1]. $^{222}$Rn can easily enter the human body through respiration system and affect lung with high energy alpha radiation as it decays. Hence, the World Health Organization recognized $^{222}$Rn as a secondary cause of lung cancer after smoking [2].

The activity concentration of $^{226}$Ra in soil from natural environment in Korea varies from 6.31 to 135 Bq · kg$^{-1}$ and averaged as 39.4 Bq · kg$^{-1}$ [3]. While in the United States, the activity concentration of $^{226}$Ra in soil are in the range of 8–160 Bq · kg$^{-1}$ with an average of 40 Bq · kg$^{-1}$ and uranium concentration in phosphate ores found to be in the range of 20–300 ppm or about 0.26–3.7 Bq · g$^{-1}$ and thorium occurs at essentially background levels, between 1–5 ppm (or about 0.0037–0.022 Bq · g$^{-1}$) [4, 5]. However, with some specific situations, the activity concentration can be enhanced by human activities such as mining and industrial activity including fertilizer production. The material with enhanced activity concentration is known as TENORM (technologically enhanced naturally occurring radioactive material). Phosphogypsum generated in fertilizer production is classified as TENORM by the United States Environmental Protection Agency [5].

Phosphogypsum is generally used for building materials such as phosphate board and cement, which may cause accumulation of indoor radon. Recently, the Korea Land & Housing Corporation established a guideline for the reduction of radioactive materials in building material [6]. According to the guideline, activity concentration of $^{226}$Ra was set for $\leq$ 130 Bq · kg$^{-1}$, as a standard of proper building material. Although phosphogypsum is no longer used in Korea as building material, some buildings using phosphogypsum constructed in the past still exist. Thus, on a regulatory perspective, the measurement method for $^{226}$Ra activity concentration still needs to be developed.

Many researches on the measurement of the $^{226}$Ra activity concentration as the source of $^{222}$Rn exhalation from the phosphogypsum have been conducted. Direct method measures 186.2 keV photon energy peak of $^{226}$Ra. However, 185.7 keV peak from $^{235}$U interrupts the peak of $^{226}$Ra, this interval between 185.7 keV and 186.2 keV is so close that even HPGe detector with good resolution cannot identify both nuclides. Thus, additional alpha spectrometry is needed to subtract the portion of $^{235}$U. Otherwise, an indirect method measures 295.0 keV of $^{214}$Pb and 609.3 keV of $^{214}$Bi peaks. This method needs to suppose that $^{226}$Ra and its daughters to be in equilibrium. Thus, to determine $^{226}$Ra precisely by this method, it takes about 28 days to achieve secular equilibrium [7].

Fig. 1. Uranium decay series [1].
To avoid these disadvantages, a research was performed to study the correction factor estimated from the natural abundance ratio of $^{238}\text{U}$ and $^{235}\text{U}$. However, the correction factor cannot be implemented on measuring $^{226}\text{Ra}$ concentration in phosphogypsum TENORM because the secular equilibrium between $^{226}\text{Ra}$ and $^{238}\text{U}$ has been interrupted [8]. Unlike natural materials, phosphogypsum as a by-product of phosphatic fertilizer is produced by chemical process that separates uranium in phosphoric acid from radium in phosphogypsum. As a result, phosphogypsum contains higher activity concentration of $^{226}\text{Ra}$ compared to its $^{238}\text{U}$ parent nuclide [9].

Furthermore, another consideration on $^{226}\text{Ra}$ measurement in indirect gamma spectrometry is $^{222}\text{Rn}$ leakage from the sample container. Since $^{222}\text{Rn}$ is an inert gas, it can easily escape from the sample container even with a tiny crack of gap between container and its lid. A research related to radon tightness of sample container in radium activity measurement of soil sample has also been done. This research using indirect method by high-purity germanium (HPGe) detector and closed-loop radon measurement method (RAD7) to determine the tightness of sample container using three different sealing methods. Marinelli beaker was used in this research, and its release fractions of the three sealing methods were obtained from the proportion of radon gas that released from the sample container to total free radon concentration potentially released to the air from soil in Marinelli beaker. This method, however, requires specific equipment to seal the container tightly [10].

Therefore, this research evokes a measurement method of $^{226}\text{Ra}$ activity concentration of phosphogypsum by gamma-spectrometry using HPGe detector where leak-correction factor is applied for compensating the radium underestimation caused by the released $^{222}\text{Rn}$ especially on the radon leaked container. Results are compared with, first, the certified value of phosphogypsum as a reference material, and second, $^{226}\text{Ra}$ activity from the phosphogypsum in properly sealed sample container.

### Materials and Methods

#### 1. Phosphogypsum Sample and Sample Container Sealing Methods

The International Atomic Energy Agency (IAEA) phosphogypsum reference material was used as a sample in this study. This sample is certified for $^{210}\text{Pb}$, $^{226}\text{Ra}$, $^{230}\text{Th}$, $^{234}\text{U}$, and $^{226}\text{U}$ nuclides as shown in Table 1. The activity concentration of the sample was certified on January 1, 2008, then activity concentration of $^{226}\text{Ra}$ once the measurement was conducted (July 1, 2019) was calculated as 776.1 ± 62 Bq·kg⁻¹ using its half-life. In this study, an indirect method is used to analyze $^{226}\text{Ra}$, therefore radioactivity concentration between $^{226}\text{Ra}$ and daughter nuclides is considered. After 21 days of measurement, daughter nuclides’ activity reaches 97.7% of the decay-calculated $^{226}\text{Ra}$ concentration (776.1 ± 62 Bq·kg⁻¹), which is 758.8 ± 61 Bq·kg⁻¹.

The physical form of the sample was powder typed that was put into 450 mL Marinelli beaker (MB) container that is widely used for gamma spectrometry with HPGe detector. The degree of tightness of the three different sealing methods (MB1, MB2, MB3) that has been studied previously were used as given in Table 2. Radon leakage from MB1 type sample container was 25%, MB2 type was 14% and MB3 type was not determined because released radon from MB3 type sample container was at the background level.

#### 2. Measurement Method

Gamma spectrometry using HPGe detector (GEM15P4; Ortec, Oak Ridge, TN, USA) was conducted to measure $^{226}\text{Ra}$ activity concentration in phosphogypsum sample. The sample was measured with HPGe detector in lead chamber which is made of 5 cm-thick lead brick to shield background gamma rays as shown in Fig. 2. Prior to sample measurement, the detector efficiency calibration was performed using a

<table>
<thead>
<tr>
<th>Table 1. Certified Value for Radionuclides in Phosphogypsum Sample</th>
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<tbody>
<tr>
<td>Radionuclide</td>
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<tr>
<td>-------------------</td>
</tr>
<tr>
<td>Lead-210 ($^{210}\text{Pb}$)</td>
</tr>
<tr>
<td>Radium-226 ($^{226}\text{Ra}$)</td>
</tr>
<tr>
<td>Thorium-230 ($^{230}\text{Th}$)</td>
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<tr>
<td>Uranium-234 ($^{234}\text{U}$)</td>
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<tr>
<td>Uranium-238 ($^{238}\text{U}$)</td>
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<thead>
<tr>
<th>Table 2. Sealing Methods and Radon Leakage Fraction of Marinelli Beaker</th>
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<tr>
<td>Sealing method</td>
</tr>
<tr>
<td>----------------</td>
</tr>
<tr>
<td>MB1 Lid without seal</td>
</tr>
<tr>
<td>MB2 Sealed with lid and paraffin film</td>
</tr>
<tr>
<td>MB3 Sealed with silicon glue and evacuated with plastic bag</td>
</tr>
</tbody>
</table>

MB, Marinelli beaker.

*From [10].*
reference material certified by the Korea Research Institute of Standards and Science (KRISS). The reference material contained multiple nuclides with gamma energy peaks range from 59.54 keV to 1,836 keV. Thereafter, the sample was sealed with the following order of MB1, MB2, and MB3 and each sealed sample was measured for 21 days continuously, data were taken for every 84,600 seconds. Phosphogypsum sample was purged after 21-day measurement to remove the $^{222}\text{Rn}$ gas that might exist in the sample. Each gamma spectrum was taken to analyze peaks of $^{226}\text{Ra}$, $^{214}\text{Pb}$, and $^{214}\text{Bi}$ after subtraction of background peaks. Background peaks were measured for 84,600 seconds with empty sample container.

Results and Discussion

1. Gamma Spectrometry Results

The HPGe detector measures gamma rays as nuclides decay in the sample. It provides gamma-ray energy spectrum so that nuclides can be identified by its energy peaks. Two daughter nuclides of $^{226}\text{Ra}$ ($^{214}\text{Pb}$ and $^{214}\text{Bi}$) emit gamma rays with high yields, i.e., 295.0 keV with 18.42% yield from $^{214}\text{Pb}$ and 609.3 keV with 45.49% yield from $^{214}\text{Bi}$. Therefore, to obtain $^{226}\text{Ra}$ activity concentration, $^{214}\text{Pb}$ and $^{214}\text{Bi}$ activity concentrations in phosphogypsum in three different sealing methods were measured by gamma spectrometry, and the
results are depicted in Fig. 3A and 3B. Some data points were missing in MB3 curve because the gamma spectrometry system lost its power for several days during the 21-day measurement.

In both Fig. 3A and 3B, daily measured values were depicted as points and that increased towards the line of certified value (776.1 ± 62 Bq · kg⁻¹) from IAEA reference material that has considered it’s decay during the period from the reference date and measured date. If there was no leak from the sample container, the measured value of the activity concentration of $^{214}$Bi and $^{210}$Pb should reach 97.7% of the certified value (758.8 ± 61 Bq · kg⁻¹) by radioactive equilibrium between radium and its daughter nuclides after 21 days from the beginning of the measurement. However, for both $^{214}$Bi and $^{214}$Pb, there were discrepancies between the measured value of 21-day and certified value, which indicates the leakage from the sample container existing in all three sealing methods.

Activity concentrations of $^{214}$Bi and $^{214}$Pb in Fig. 3A and 3B resulted during the measurement period show that concentrations of both nuclides were built-up and saturated in the sample container. Daily measured activity concentrations were fitted with Origin 2018 program to analyze the saturated value and compared to the IAEA certified value. Saturated values of $^{214}$Bi were 665.7 ± 1.3 Bq · kg⁻¹, 670.2 ± 1.4 Bq · kg⁻¹, and 713.9 ± 2.0 Bq · kg⁻¹, respectively for MB1, MB2, and MB3, while saturated values of $^{214}$Pb were 681.9 ± 1.6 Bq · kg⁻¹, 689.3 ± 2.0 Bq · kg⁻¹, and 735.4 ± 2.7 Bq · kg⁻¹, respectively on MB1, MB2, and MB3. The result of both $^{214}$Bi and $^{214}$Pb showed that as the sealing of the container gets tighter, the radon leakage reduced. Especially on the MB3 sealing method, saturated value of $^{214}$Bi had 8% difference from certified value of $^{226}$Ra of phosphogypsum sample that is within the uncertainty bound. In the same way, $^{214}$Pb had 5% difference from certified value that is also within the uncertainty bound while other sealing methods showed more than 10% differences that are outside the uncertainty bound.

The result above indicates that MB3 is the proper sealing method that can be used to measure $^{226}$Ra activity concentration in phosphogypsum sample with an indirect method of HPGe gamma spectrometry. The measurement result of $^{214}$Bi was slightly less than $^{214}$Pb and that cause larger difference to compare with the certified value. It is due to the $^{214}$Bi result needs to be corrected, related to its true coincident summing effect to prevent underestimation of its activity concentration [11]. Thus, in this study, $^{214}$Pb was used to analyze $^{226}$Ra concentration.

The measurement results also show that $^{226}$Ra activity concentration is smaller than certified value in MB1 and MB2 due to $^{222}$Rn leakage. $^{222}$Rn is an inert gas that is easy to escape through the tiny space of sample container without reaction with other materials. The ratio of radon leakage or radon leakage fraction, as shown in Table 2, is the physical characteristics of container that is not affected by sample activity. Thus, radon leakage fraction can be used to correct $^{222}$Rn leakage of the phosphogypsum sample in this study. To compensate the leaked portion of measured value, some assumptions are used and explained in leakage correction method.

### 2. Leakage Correction Method

Taking the advantage of secular equilibrium properties between $^{226}$Ra and $^{222}$Rn, in this study, $^{226}$Ra activity concentration was obtained by adding up the non-leaked and leaked concentration of radon from the sample container. The non-leaked radon was represented by its daughter ($^{214}$Pb, $^{214}$Bi) saturated activity concentration measured by HPGe, further defined as measured activity concentration, while the leaked radon was estimated using equations below. The leaked radon is further defined as estimated activity concentration. The estimation of leaked radon is based on an assumption that leaked $^{222}$Rn gas establishes secular radioactive equilibrium with $^{214}$Pb or $^{214}$Bi in a space with a certain volume. If $N_2$ is the number of radon daughter nuclide atoms, then the rate of change for radon daughter nuclides can be expressed with generation term and decay term as shown in the following differential equation:

$$\frac{dN_2(t)}{dt} = k\lambda_1 N_1 - \lambda_2 N_2 \tag{1}$$

where $N_1$ is the number of $^{222}$Rn atoms, $\lambda_1$ and $\lambda_2$ are decay coefficient of $^{222}$Rn and $^{214}$Pb, respectively, and $k$ is radon leakage fraction of Marinelli beaker as given in Table 2 that represents a leak proportion of radon gas from the sample container. For MB1, MB2, and MB3, $k$ value was 0.25, 0.14, and about 0 which showed background level that can be neglected.

By solving Equation (1), $N_2(t)$ can be derived as follows:

$$N_2(t) = \frac{k\lambda_1 N_1(0)}{\lambda_2 - \lambda_1} \left( e^{-k\lambda_1 t} - e^{-\lambda_2 t} \right) \tag{2}$$

where $N_1(0)$ indicates an initial value of the number of $^{222}$Rn atoms, which is the first 86,400 seconds measured value of
radon daughter activity concentration in this study. Because the decay constant is 19.9 minutes for $^{214}\text{Bi}$ and 26.8 minutes for $^{214}\text{Pb}$ then it can be assumed that $^{222}\text{Rn}$ and its daughter nuclides are in equilibrium. Thus, $A_2(t)$, activity of radon daughter nuclides, can be obtained by multiplying $\lambda_2$ to Equation (2).

$$A_2(t) = \frac{k\lambda_1 \lambda_2 N(t)}{\lambda_2 - \lambda_1} (e^{-k\lambda_1 t} - e^{-\lambda_2 t}) \tag{3}$$

The radon leakage fraction ($k$) in Equation (1) to (3) indicates that if the sample container is sealed perfectly and no radon leaked ($k=0$), then the estimated activity concentration ($A_2$) will be zero, then the total activity concentration will be equal to the measured activity, which shows an ideal container sealing condition.

### 3. Correction Result

Results of $^{226}\text{Ra}$ activity concentration using leak correction method are presented in Table 3 with used parameters. Estimated activity concentration was obtained from the Equation (1) to (3) that represents leaked portion of $^{222}\text{Rn}$ gas from sample container and measured activity concentration was obtained from indirect gamma spectrometry that represents saturated $^{222}\text{Rn}$ gas in sample container. Besides, leakage-corrected $^{226}\text{Ra}$ activity concentration that is the summation of estimated and measured activity concentration of $^{226}\text{Ra}$ is also shown in Table 3. Also, leakage-corrected $^{226}\text{Ra}$ activity concentration was compared with certified $^{226}\text{Ra}$ activity concentration of IAEA reference material and the difference between them was calculated.

Results demonstrate that MB2 is tighter sealing method than MB1 as estimated results of MB1 were higher than MB2 and measured results were smaller in both $^{214}\text{Bi}$ and $^{214}\text{Pb}$ commonly. However, results of $^{214}\text{Bi}$ total activity concentration showed small discrepancy from certified values, because of coincident summing effect was not considered in this study, while results of $^{214}\text{Pb}$ total activity concentration showed almost correspondence with certified value with about 2%.

Thus, it can be concluded that a proper method for determining $^{226}\text{Ra}$ activity concentration is introduced in this study when the indirect method of gamma spectrometry using $^{214}\text{Pb}$ energy peaks with leak correction method is used. This method only requires a Marinelli beaker and an initial measurement value for calculation and the measurement value of 21-day. Nonetheless, this result is specific for the Marinelli beaker as sample container, while for other sample containers, a new radon leakage fraction is required. For further study, coincidence summing effect of $^{214}\text{Bi}$ will be considered for radon leak correction method.

### Conclusion

In this study, the activity concentration of $^{226}\text{Ra}$ in the phosphogypsum, TENORM from fertilizer industry, sample was measured using HPGe gamma spectrometry. Determining $^{226}\text{Ra}$ in phosphogypsum has many challenges such as interruption of 186.2 keV $^{235}\text{U}$ gamma peak to its peak in direct measurement, and interruption of radioactive secular equilibrium between $^{238}\text{U}$ and $^{226}\text{Ra}$ by radon leakage from the sample container. Therefore, in this study, a proper measurement method for determining $^{226}\text{Ra}$ using indirect gamma spectrometry combined with radon leakage correction method for different sealing method of sample container was studied.

Measurement results of indirect method using $^{226}\text{Ra}$ daughter nuclides ($^{214}\text{Bi}$ and $^{214}\text{Pb}$) showed continuous build-up and saturation of $^{222}\text{Rn}$ in the phosphogypsum sample. Activity concentration in MB3 sealing method showed very close value to the IAEA certified value while the results of MB1 and MB2 cases had discrepancy from the certified value in both $^{214}\text{Bi}$ and $^{214}\text{Pb}$. The discrepancy was caused by the

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**Table 3. Results of $^{226}\text{Ra}$ Activity Concentration Using Leakage Correction Method and Gamma Spectrometry for $^{214}\text{Bi}$ and $^{214}\text{Pb}$**

<table>
<thead>
<tr>
<th></th>
<th>$k$ (day$^{-1}$)</th>
<th>$\lambda_1$ (day$^{-1}$)</th>
<th>$\lambda_2$ (day$^{-1}$)</th>
<th>$^{226}\text{Ra}$ activity concentration (Bq·kg$^{-1}$)</th>
<th>Difference (%)</th>
<th>Leakage corrected (C)</th>
<th>Certified (D)</th>
</tr>
</thead>
<tbody>
<tr>
<td>$^{214}\text{Bi}$</td>
<td></td>
<td></td>
<td></td>
<td>Estimated (A)</td>
<td></td>
<td>Measured (B)</td>
<td></td>
</tr>
<tr>
<td>MB1</td>
<td>0.25</td>
<td>0.181</td>
<td>37.2</td>
<td>57.7 ± 3.8</td>
<td>0.3</td>
<td>665.7 ± 1.3</td>
<td>723.4 ± 4.0</td>
</tr>
<tr>
<td>MB2</td>
<td>0.14</td>
<td></td>
<td></td>
<td>49.0 ± 3.2</td>
<td>0.5</td>
<td>670.2 ± 1.4</td>
<td>719.2 ± 3.5</td>
</tr>
<tr>
<td>$^{214}\text{Pb}$</td>
<td></td>
<td></td>
<td></td>
<td>60.0 ± 3.2</td>
<td>0.3</td>
<td>681.9 ± 1.6</td>
<td>741.9 ± 3.6</td>
</tr>
</tbody>
</table>

$\text{Bi}$, bismuth; $\text{Pb}$, lead; MB, Marinelli beaker.

$C = A+B, E = \frac{D-C}{D}$.
leaked radon, therefore leak correction was added to the indirect gamma spectrometry to obtain the 226 Ra activity concentration.

Total activity concentration of 226 Ra obtained from measured and calculated results of leak correction method. Results using 214 Bi peaks were 723.4 ± 4.0 Bq·kg⁻¹ in MB1 and 719.2 ± 3.5 Bq·kg⁻¹ in MB2 that showed discrepancy of about 5% compared to the certified activity. Besides, results using 214 Pb peaks were 741.9 ± 3.6 Bq·kg⁻¹ in MB1 and 740.1 ± 3.4 Bq·kg⁻¹ in MB2 that showed about 2% differences compared to the certified activity.

Therefore, measuring 226 Ra activity concentration in TENORM sample using radon leakage correction can be concluded as a convenient and accurate method that can be easily conducted with simple calculation. For further research, true coincidence summing effect can be corrected with Monte Carlo N-Particle (MCNP) simulation to acquire accurate results of 214 Bi peaks.

**Conflict of Interest**

No potential conflict of interest relevant to this article was reported.

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**Author Contribution**

Conceptualization: Lim S. Data curation: Lim S, Syam N. Formal analysis: Lim S, Syam N. Funding acquisition: Lee SH. Methodology: Lim S, Syam N. Project administration: Syam N, Lee SH. Visualization: Lim S. Writing - original draft: Lim S. Writing - review & editing: Maeng S, Lee SH. Resources: Syam N. Supervision: Syam N, Maeng S. Validation: Lim S, Syam N, Maeng S.

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