Identification of Pure Beta Nuclides with Very Near Maximum Energies Using a GM Counter and Thin Absorbers

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A method for identifying \(^{14}\)C from \(^{35}\)S having very near maximum energies was devised by using a GM counter and thin absorbers. Differentiation was conducted by using attenuation rates of \(^{14}\)C and \(^{35}\)S in a low energy region without determining their maximum ranges. \(^{35}\)S can be discriminated from \(^{14}\)C by measuring twice.

Key words: discrimination between \(^{14}\)C and \(^{35}\)S; GM counter; thin absorber, attenuation

1. Introduction

Pure \(\beta\) emitting nuclides such as \(^{14}\)C and \(^{35}\)S are used as tracers in a wide variety of fields such as biology, medicine, physics and chemistry. Identification of nuclide is essential for estimating surface contamination density and/or for classifying solid state wastes at radiation facilities using these radionuclides.

\(^{14}\)C with a half-life of 5,730 y emits \(\beta\)-rays having a maximum energy (\(E_{\text{max}}\)) of 156.5 keV. \(^{35}\)S with a half-life of 87.5 d emits \(\beta\)-rays having an \(E_{\text{max}}\) of 167.18 keV.

Liquid scintillation counters (LSCs) are used universally to measure the aforementioned low energy \(\beta\)-ray emitters. It is difficult to identify the nuclides as \(^{14}\)C or \(^{35}\)S in unknown samples by using LSCs, because the \(E_{\text{max}}\) difference between \(^{14}\)C and \(^{35}\)S can be as small as 10.7 keV. Four special methods using LSCs may be applied to identify the nuclides \(^{14}\)C or \(^{35}\)S. The first method utilizes half-life differences due to \(^{35}\)S’s rapid decay as compared to \(^{14}\)C. It takes about three months corresponding to the half-life of \(^{35}\)S before determining whether a sample is \(^{14}\)C or \(^{35}\)S. However, it is usually essential to identify radionuclides immediately after contamination checks, although this method is considered to be both reliable and simple. The three month requirement to complete this assay rules out its use as a routine procedure.

The other three methods such as the spectral dilatation-interpolation method, the double quench parameter curve method, and the combustion method are generally not used in routine contamination checks because of their complicated procedures. Moreover, the LSC method inevitably results in the production of radioactive liquid scintillation cocktails, which must be burned as radioactive organic wastes.

\(^{14}\)C can be discriminated from \(^{35}\)S by using their \(E_{\text{max}}\). The Feather analysis method and the spectrometer method can be used to determine the \(E_{\text{max}}\). The Feather method determines the \(E_{\text{max}}\) by extrapolating attenuation curves. The spectrometer method also determines the \(E_{\text{max}}\) by extrapolating Currie plot or Fermi plot or energy spectra. Both methods, however, require smear samples showing considerably higher count rates than background count rates around the \(E_{\text{max}}\). Typical count rates of the smear samples over the whole energy spectra are at most several times those of the background. The count rates around the \(E_{\text{max}}\) are comparable to the background count rate proximate to the \(E_{\text{max}}\). The count rates of the smear samples are too low to determine the \(E_{\text{max}}\). Additionally, sample preparation for spectrometry takes a long time because radionuclides must be
chemically extracted from the smear samples. These methods could not be routinely used to measure the smear samples.

The above conditions necessitate developing an alternative method that can be applied to routine contamination checks without producing additional wastes.

Inspection of beta-ray energy spectrum shapes of $^{14}$C and $^{35}$S indicates that a ratio of the low energy region to the whole spectrum of $^{14}$C is greater than that of $^{35}$S. Therefore, an attenuation curve of $^{14}$C must lie under $^{35}$S because a relatively large number of $^{14}$C beta-rays are absorbed by a thin absorbent layer compared with $^{35}$S. This deduction suggests the possibility of developing a method that can discriminate between $^{14}$C and $^{35}$S by comparing attenuation rates in the low energy region. It is expected that this method will be able to more efficiently detect lower activities than those methods determining the $E_{\text{max}}$, because there exist a large number of beta-rays in the low energy region when compared to the number of the same rays near the $E_{\text{max}}$.

The objective of this paper is to show that $^{14}$C can be discriminated from $^{35}$S by comparing the attenuation rates measured with a GM counter and thin absorbers.

2. Materials and methods

2.1 Materials

Figure 1 shows dimensions of an absorber and a source support. The thickness of the polyvinylidene chloride film used as absorbers was $1.83 \pm 0.014 \text{ mg cm}^{-2}$ $(9.6 \times 10^{-5} \text{ cm})$. The film was mounted on a 0.60 mm thick, 50 mm square cardboard frame having an aperture of $34 \times 24 \text{ mm}$. Twenty one absorbers were prepared by piling the film. The absorbers $A_i$ $(i=0-21)$ consisted of $i$ sheets of the polyvinylidene chloride film. Absorber $A_0$ had no film.

$^{32}$P sources were prepared by diluting $\gamma$-[3P]-ATP of 9.25 MBq (Amersham Biosciences; 370 kBq $\cdot \mu \text{L}^{-1}$). The $^{32}$P sources were used for deciding the resolving time of a GM counter and for making a Feather analyzer.

Original solutions of $^{14}$C and $^{35}$S were 1.85 MBq Benzyl $[^{14}\text{C}]$ penicillin potassium (Amersham Biosciences; 18.5 kBq $\cdot \mu \text{L}^{-1}$) and 37 MBq L-[35S] methionine (Amersham Biosciences ; 370 kBq $\cdot \mu \text{L}^{-1}$), respectively. Diluents were prepared by using non radioactive Benzyl penicillin potassium and L-Methionine, respectively.

Fifteen diluted solutions differing in activity density for both $^{14}$C and $^{35}$S were prepared from the original solutions. The activity densities of the diluted solutions from No.1 to No.15 ranged from 6.0 kBq $\cdot \mu \text{L}^{-1}$ to 1.1 Bq $\cdot \mu \text{L}^{-1}$.

A 2.0 $\pm$ 0.30 mg $\cdot \text{cm}^{-2}$ thick mica film mounted on the cardboard frame was used as a source support. A solution of 5 $\mu \text{L}$ was spotted at the center of the mica film and dried overnight in a draft chamber. The cardboard was then covered with Mylar film (DUPONT, 0.25 mg $\cdot \text{cm}^{-2}$ $(2.0 \times 10^{-4} \text{ cm}))$ and used as a source. Fifteen sources for both $^{14}$C and $^{35}$S were prepared from the solutions. The source activities ranged from 30 kBq of No.1 source to 5.5 Bq of No.15 source.

2.2 Measurement

Figure 2 shows a geometrical arrangement of a source support, an absorber and a GM tube. A 5 cm diameter GM tube with a 2.70 $\pm$ 0.05 mg $\cdot \text{cm}^{-2}$ thick mica end-window (ALOKA, GM 5004) was used. A 55 mg $\cdot \text{cm}^{-2}$ thick aluminum plate having a 2.5 cm diameter hole was placed under the end-window. The room temperature was 27°C, and
the humidity ranged from 25 to 35%. The air density under this condition was 1.42 mg·cm⁻³ within an uncertainty of 0.1%. A thickness of 1.12 mg·cm⁻² was obtained by multiplying the air density by the aerial layer of 0.79 cm between the source and the end-window.

When an absorber was inserted between the GM tube and the sources, the thickness of the aerial layer between the GM tube and the sources was reduced by the thickness of the absorber consisting of polyvinylidene chloride film and the mylar film. The aerial layer thickness \( T_a \) in cm corresponding to two materials is given by the relationship

\[
T_a = 9.6 \times 10^{-5} \cdot i + 2.0 \times 10^{-4} \text{ cm}
\]

Let \( T_s \) in mg·cm⁻² be the sum of the thicknesses of the end-window (2.70 mg·cm⁻²), Mylar film (0.25 mg·cm⁻²), absorber \( A_i \) (1.83·i mg·cm⁻²), and aerial layer (1.12 mg·cm⁻²). When absorber \( A_i \) was inserted, the total thickness of absorption layer \( L_{t} \) in mg·cm⁻² was obtained by subtracting \( T_s \) in mg·cm⁻² from \( T_a \).

\[
L_t (\text{mg·cm}^{-2}) = T_a - T_s = (2.70 + 0.25 + 1.83 \cdot i + 1.12) - 1.42 \times (9.6 \times 10^{-5} \cdot i + 2.0 \times 10^{-4}) = 4.07 + 1.83 \cdot i \text{ mg·cm}^{-2}
\]

(1)

Attenuation rates were measured in accordance with the Feather analysis method. Each attenuation rate was measured 5 times, and the average of the five rates was referred to as the attenuation rate. Each measurement time was adjusted to 0.1 – 50 min so that the count was greater than 1,000.

A resolving time of 3.9×10⁻⁴ sec was preliminary determined with a 420 Bq \(^{32}\)P source in accordance with the two-source method. Dead time loss was corrected by using the resolving time. Net counts were obtained by subtracting the background (BG) counts from the raw counts.

Both the mica and the Mylar sheets were removed from the cardboard frames after attenuation rates were measured and then put into vials where liquid scintillation cocktails were added (Amersham Biosciences Corp.: ACS II). The activities of \(^{14}\)C and \(^{35}\)S were determined by using an LSC (BECKMAN LS6500). The counting efficiencies of the GM counter were calculated by dividing the net count rates by the activities.

### 2.3 Identification of the nuclide

#### Attenuation curve

Attenuation curves were obtained in accordance with the Feather analysis method. A measured attenuation curve was interpolated to the absorber thickness of 0 mg·cm⁻² and normalized to the interpolated value \( C_{0R} \). The attenuation rates of bremsstrahlung in the thickness beyond a maximum \( \beta \)-ray range were simulated by a straight line. A net attenuation curve was obtained by once again normalizing the
attenuation curve obtained by subtracting the straight line from the normalized attenuation curve.

**Criteria for identifying a nuclide as \(^{14}\text{C}\) or \(^{35}\text{S}\)**

The net attenuation curves in the range from \(L_0\) to \(L_4\) corresponding to low energy region were fitted to exponential functions by means of the least-square method. The functions for \(^{14}\text{C}\) and \(^{35}\text{S}\) were noted as \(y_c\) and \(y_s\), respectively.

Suppose an unknown sample contains either \(^{14}\text{C}\) or \(^{35}\text{S}\). Let the count rate obtained with absorber \(A_i\) be \(C_i\) (cpm). The attenuation rate \(Y(\%)\) is given by equation (2).

\[
Y(\%) = (C_i \times C_{0i}^{-1} \times 100) \times 100 \times C_{ei}^{-1}
\]

(2)

It was confirmed by preliminary experiments that the attenuation rates of \(^{14}\text{C}\) were lower than those of \(^{35}\text{S}\). Let a standard deviation of \(Y\) be \(\sigma\). The unknown source was determined to be \(^{14}\text{C}\) when \(Y\) coincides with \(y_c\) within \(\pm 10\%\), and \(Y + 3\sigma\) is smaller than 0.9\(y_c\), as given in eq.(3). Contrarily the unknown source was determined to be \(^{35}\text{S}\) when \(Y\) coincides with \(y_s\) within \(\pm 10\%\), and \(Y - 3\sigma\) is larger than 1.1\(y_s\), as given in eq.(4).

\[
0.9y_c < Y < 1.1y_c, \quad Y + 3\sigma < 0.9y_c, \quad (3)
\]

\[
0.9y_s < Y < 1.1y_s, \quad Y - 3\sigma > 1.1y_s, \quad (4)
\]

These relationships were used as criteria for discriminating \(^{14}\text{C}\) from \(^{35}\text{S}\). Minimum activities meeting relationship (3) or (4) were termed the lowest identifiable activities (LIA's) for \(^{14}\text{C}\) or \(^{35}\text{S}\). The attenuation rates can be determined by measuring the rates twice with two absorbers. The LIA's four combinations were calculated for absorber \(A_0\) and absorbers \(A_1\) to \(A_4\).

Minimum detectable activity (MDA) was calculated by using the counting efficiency and \(3\sigma\) under conditions that samples and BG were measured for the same period of time. The LIA is logically greater than the MDA because \(^{14}\text{C}\) or \(^{35}\text{S}\) is identified after detecting radioactivity.

The LIA and the MDA were compared with 40 Bq corresponding to the legal surface limit in controlled area (legal surface limit) and 4 Bq equivalent to the legal goods limit that are permitted to be carried away from the controlled area (legal goods limit) in Japan.

**3. Results**

Figure 3 shows the net attenuation curves between \(L_0\) and \(L_4\). The attenuation curves of \(^{14}\text{C}\) and \(^{35}\text{S}\) were approximated by the following exponential functions (5) and (6):

\[
y_c = 111e^{-0.326x}, \quad (5)
\]

\[
y_s = 113e^{-0.3011x}, \quad (6)
\]

where \(x\) is the absorber thickness from 4.1 to 11.4 mg·cm\(^{-2}\). The eqs. (5) and (6) coincided with the net attenuation curves of \(^{14}\text{C}\) less than an error of \(\pm 0.7\%\), and \(^{35}\text{S}\) less than an error of \(\pm 1.6\%\). The bremsstrahlung percentages of the net attenuation rates for \(^{14}\text{C}\) and \(^{35}\text{S}\) were about 0.02% at \(L_0\), 0.2% at \(L_4\), and 0.4% at \(L_0\).

Table 1 shows counting efficiencies of the GM counter for \(^{14}\text{C}\) and \(^{35}\text{S}\) when absorbers from \(A_0\) to \(A_4\) were used. The
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Fig. 4. Attenuation curve (Y) of the 150 Bq $^{35}$S measured for 5 min. $y_c$ and $y_s$: Approximate functions of the net attenuation curves of $^{14}$C and $^{35}$S, respectively. Error bars show $3\sigma$.

Figure 4 shows a net attenuation curve of a 150 Bq $^{35}$S source. Error bars designate $3\sigma$. The values of Y were larger than 0.9$y_c$ and smaller than 1.1$y_s$. Every $Y-3\sigma$ was larger than 1.1$y_c$. All attenuation rates at $L_0-L_4$ satisfied the equation (5). The 150 Bq $^{35}$S was discriminated from $^{14}$C by measuring attenuation rates at $L_0$ without absorber and at $L_i$ ($i=1-4$) with absorber.

The percentage of the bremsstrahlung in the normalized attenuation curves between $L_0$ and $L_4$ was less than an error of 0.2%.

Figure 5 shows the relationships between the lowest identifiable activity (LIA) and the measurement time when $^{14}$C was measured for 300 min. When the absorber $A_1$ was used, the LIA of $^{14}$C decreased from 450 to 24 Bq as the measurement time increased from 1 to 50 min. The LIAs of $^{14}$C and $^{35}$S were less than the legal limit of 40 Bq in the controlled area when the samples were measured for 20 min or longer. Contrasting, when absorber $A_4$ was used, the LIAs were greater than the legal surface density limit up to 50 min. The thinner absorbers gave smaller LIAs. The $^{35}$S LIAs were lower than $^{14}$C except for a 3 min measurement with absorber $A_3$.

Counting efficiencies of $^{14}$C and $^{35}$S ranged from 5.0 to 0.53% and from 5.6 to 0.76%. The counting efficiencies of $^{35}$S were larger than $^{14}$C. The difference between counting efficiencies decreased gradually when the absorber thickness increased.

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Figure 6 shows the relationships between the minimum detectable activity (MDA) and the measurement time. The MDAs were calculated by using the counting efficiencies shown in Table 1. The MDAs decreased as the measurement time increased. The MDAs of $^{35}$S were lower than $^{14}$C when the same absorbers were used. The MDA increased when the absorber thickness increased from $A_0$ to $A_4$. When the absorber $A_0$ was used, the MDAs of both $^{14}$C and $^{35}$S showed the lowest values. The MDAs of $^{14}$C and $^{35}$S for a 1 min measurement were about 9 and 10 Bq, respectively, and they were less than the legal surface limit of 40 Bq. The respective MDAs of $^{14}$C and $^{35}$S for a 7 min measurement were 3.7 and 3.3 Bq, and they were lower than the legal limit for goods of 4 Bq.

4. Discussion

Identification of the nuclides in samples containing $^{14}$C or $^{35}$S was attained by using a GM counter and thin absorbers without determining the maximum range of beta rays. This method utilized the difference between the attenuation rates of $^{14}$C and $^{35}$S in a low energy region. Basically the difference of the count rate ratios $C_1/C_0^{-1}$ between $^{14}$C and $^{35}$S can be used to identify the nuclides instead of the normalized attenuation rate $Y(\%)$ as shown in eq.(2). Larger difference makes it possible to identify smaller activity. Both ratios, however, reach to a value 1 as the thinner $A_4$ is used, and the difference between the ratios decreases considerably. Resultantly, the identifiable activity will show extremely high value. The normalization in eq.(2) resolved this problem by enlarging the difference between attenuation rates. The normalization was conducted.

The difference of the attenuation rates became maximal as shown in Fig.3 when a combination of $A_0$ and $A_1$ was used. Consequently, the lowest identifiable activities (LIAs) were obtained by measuring the count rates twice at $L_0$ with $A_0$ and at $L_1$ with the thinnest absorber $A_1$.

The identifiable activities were estimated by using the count rate ratios in eq. (2). The ratios varied depending on the thickness of the absorber and the GM tube’s end-window. A combination of a commercially available GM tube and thin film was used in this study. An optimal combination to maximize the identifiable activities should be revealed by the further investigation.

The method for identifying the nuclides as $^{14}$C or $^{35}$S using GM counters have the following advantages: (1) counting efficiency for $\beta$-rays is high; (2) chemical treatment is not required for sample preparation; (3) no additional radioactive waste is generated aside from the smear samples. The identification method using the GM tubes greatly contributes to radiation safety management as well as the radiation measurement technology.

The influence of the bremsstrahlung on the normalized
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attenuation curves between L₀ and L₄ was less than an error of 0.2%. The normalized curves in this region can be regarded as the net attenuation curves within an error of 0.2%; thus the normalized curves can be applied for analyzing the attenuation rates instead of the net curves.

When a sample of ¹⁴C was measured with two absorbers A₀ and A₁ for 10 min, the LIA and MDA were estimated to be about 50 Bq as shown in Fig.5 and 3 Bq as shown in Fig.6, respectively. The MDA ranged from 1/16 to 1/4 of the LIA when MDAs in Fig.5 were compared with the LIA in Fig.6. The MDA was roughly 1/10 of the LIA. Generally, an activity of a nuclide contained in an unknown sample should be determined by using a count obtained with the absorber A₀ after identifying the nuclide by using two absorbers A₀ and A₁. This method is simple and has enough sensitivity for detecting the legal surface limit; therefore the method can be used in routine contamination checks.

5. Conclusion

Discrimination between ¹⁴C and ³⁵S was realized by using a GM counter and thin absorbers without determining the maximum ranges of beta rays. Attenuation curves of ¹⁴C and ³⁵S in a low energy region were used to discriminate between these two radionuclides. Identification can be carried out by measuring the attenuation rates twice. Differentiating ¹⁴C from ³⁵S having activity equal to the legal surface limit of 40 Bq can be carried out by making 20 min or longer measurements.

References

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