LIGHT YIELDS AND PULSE-HEIGHT SPECTRA OF HIGH-PURITY TEFLON VIALS FOR ACCURATE ^{14}C MEASUREMENT IN OLD TREE RINGS

W Kato • H Sakurai[1] • K Suzuki • Y Takahashi • T Gandou • N Agatsuma • S Gunji • F Tokanai

Department of Physics, Yamagata University, 1-4-12 Kojirakawa, Yamagata 990-8560, Japan.

ABSTRACT. Seventy-eight high-purity Teflon® copper counting vials (20 mL) were investigated for weight, light yield, and background counting rate in order to prepare many vials of the same quality with high light yields for accurate radiocarbon single-year measurements of old tree rings. The relative standard deviations of the container weights and the copper cap weights are 1.7% and 0.75%, respectively. The light yields of the vials investigated with spectral quench parameter (SQP) values using dead benzene (DB) indicate a small positive correlation between the SQP values and the container weights, indicating a small increase in light yield. The average background counting rate is 0.086 cpm/g DB, with a standard deviation of 0.0045 for all vials; thus, there are no vials with serious radioactive impurities for any lots. The validity of the normalizing method was ensured using 3 types of vials with different SQP values and ~30 g of equal-quality benzene (CB).

INTRODUCTION

Solar activities are detectable in terrestrial materials as a variation in the quantity of cosmogenic radionuclides. The 11-yr periodicity of solar activity is a key point for investigating past cosmic rays and solar activities. Cosmogenic radionuclides produced by cosmic rays coming to Earth are modulated with 11-yr periodicity by the magnetic fields in the heliosphere originating from solar activities. Thus, radiocarbon measurements of single-year tree rings of old wood samples are essential for investigating the periodicity of past solar activity, because tree rings guarantee a time resolution of a single year.

We measured ^{14}C in single-year tree rings of a ~2500-yr-old cedar to investigate the 11-yr periodicity of solar activity in the distant past (i.e. >2000 yr ago) (Sakurai et al. 2003a, 2004; Gandou et al. 2004). As the expected modulation of the ^{14}C concentrations is <1%, it is necessary to measure the rings with good accuracy. Our highly accurate ^{14}C measuring system is composed of a benzene synthesizer, which is capable of producing a large quantity (10.5 g) of benzene, and a Quantulus 1220™ liquid scintillation counting system. The accuracy is <0.2% for ^{14}C measurements of single-year tree rings. A benzene sample is synthesized from CO_2 produced by burning the cellulose extracted chemically from the tree rings. The benzene sample is placed in a high-purity Teflon® copper vial (Wallac Oy) and then measured with the Quantulus.

Since each benzene sample is contained in a vial when measured, it is very important to prepare uniform vials for light yield (Sakurai et al. 2003b). The Quantulus has an indicator to monitor the yield of scintillation light from benzene contained in a vial (spectral quench parameter [SQP]) when irradiated by external gamma rays from a radioisotope. The light yields of blank vials were determined from the SQP using commercially manufactured dead benzene for selecting the vial.

Finally, to determine ^{14}C concentrations for single-year tree rings with high accuracy, we developed a normalizing method for counts from vials with different SQP values, relative to standard benzene produced from oxalic acid by NIST, and employing the pulse-height spectrum of ^{14}C. This normalization indicates that the counts are consistent to <0.2% for the same ^{14}C benzene with different SQPs.

We describe the light yields of the high-purity Teflon vials as well as the normalization method.

[1]Corresponding author. Email: sakurai@sci.kj.yamagata-u.ac.jp.

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Light Yields of Teflon Vials

Seventy-eight high-purity Teflon copper counting vials (20 mL) manufactured by Wallac Oy were investigated for weight, light yield, and background counting rate. The vials were measured for the total weight of the Teflon container including the copper cap and the vial container weight (excluding the copper cap), with an accuracy of 0.1 mg. The copper cap weight was calculated by subtracting the vial weight from the total weight. As shown in Table 1, the relative standard deviations of the container weights and the copper cap weights are 1.7% and 0.75%, respectively. The Teflon containers vary in weight at nearly double the rate for the copper caps (standard deviation of 1.7% to 0.75%); this may be due to slight differences in production, leading to small weight fluctuations in the Teflon containers. In fact, as shown in Figure 1, the distribution of the container weights is not a statistical distribution (e.g. Gaussian distribution), and shows a difference of ~1 g between the maximum and minimum.

Table 1 Weights of high-purity Teflon copper counting vials.

	Total weight	Container weight	Copper cap weight
Average weight (g)	54.3373	13.7105	40.6268
Standard deviation (SD)	0.46	0.24	0.30
Relative SD (%)	0.84	1.7	0.75

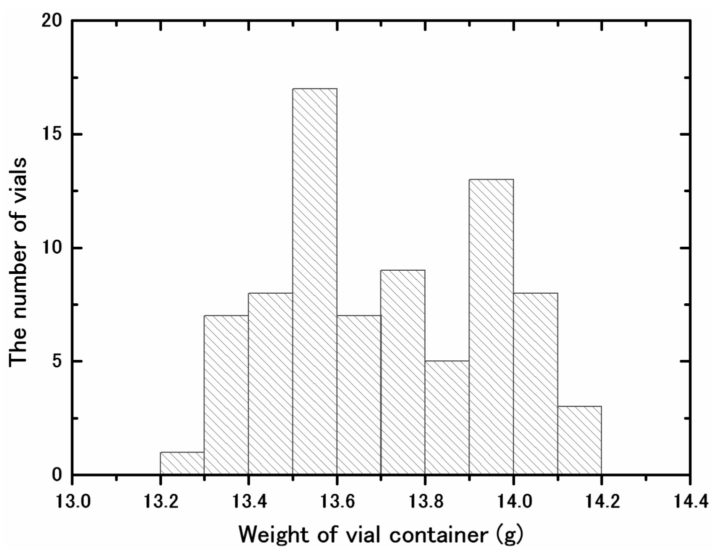

Figure 1 Distribution of vial container weights

The light yields of blank vials were determined by the SQP using 10.5 g of commercially manufactured dead benzene (DB) with added butyl-PBD (15 mg/mL) as the scintillator (standard deviations of 0.15% and 0.78%, respectively). The same proportions were used for the benzene samples produced from the tree rings. Using the same quantities of DB and scintillator in the blank vials allows for a detailed investigation of characteristics of individual vials under the same conditions.

Figure 2 shows the SQP values for each vial. As the vial number roughly represents the time of purchase, the difference between the SQP values might indicate the difference between lots in the manufacturing process. In Figure 3, the distribution of SQP values for each vial averages an SQP value of 891.1 channels, with a standard deviation of 2.9 channels. As the SQP value is the average of 12 irradiations and the standard deviation is 1.2 channels, the distribution of SQP values is more spread out than that of statistical behavior. If the spread is caused by a systematic fluctuation of the Teflon thickness, we may find a correlation between the SQP value and the container weight. Figure 4 shows a scatter plot of SQP values and the container weights of each vial. In the figure, a straight line indicates the least-squares-fitted line, and the gradient is an increase of 2.3 channels per 1 g Teflon vial weight. Although the correlation is not very clear, the trend implies that the Teflon material influences the diffusion of scintillation light and hence causes a small increase in light yield. However, since for any container weight of 13.2–14.2 g the SQP values fluctuate in the width of ~5 channels, other factors (e.g. a small differences in the form of the vials) are presumably more important than the container weight for the light yield fluctuation of each vial.

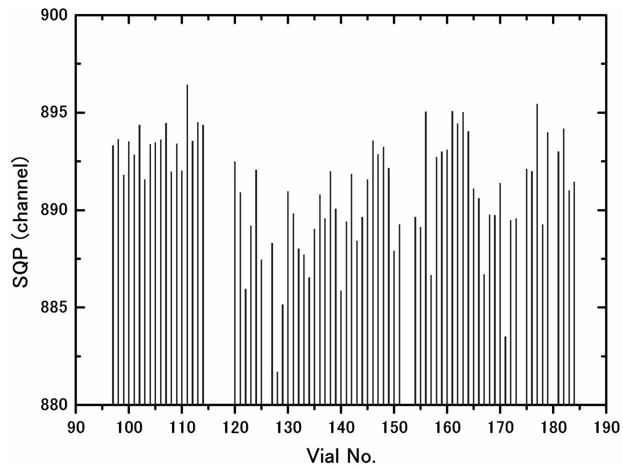

Figure 2 SQP values for 78 vials

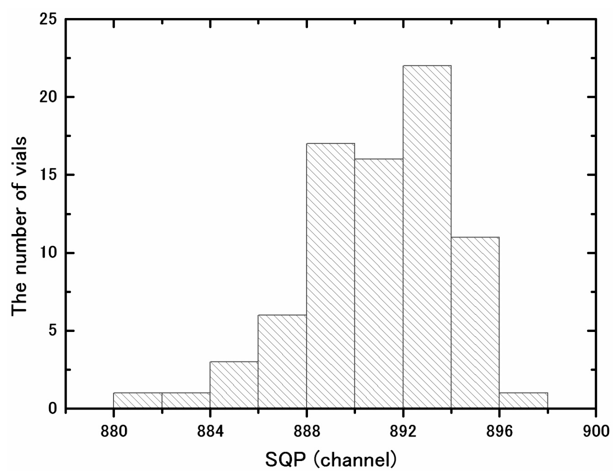

Figure 3 Distribution of light yields of vials

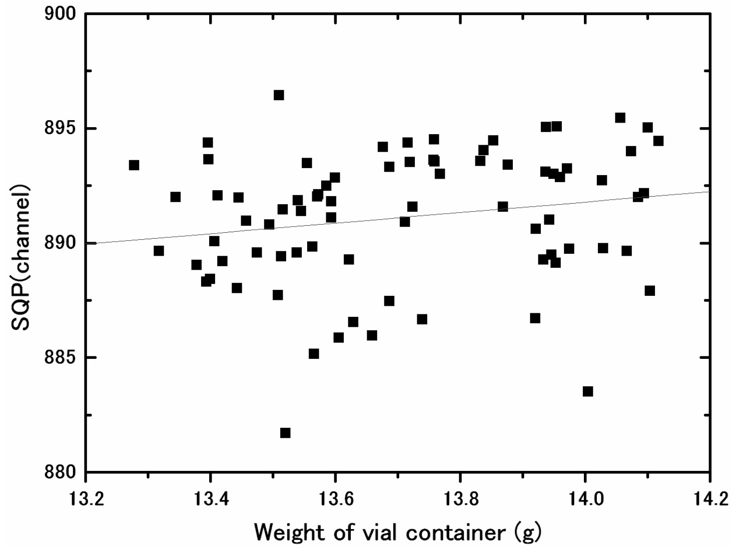

Figure 4 Correlation between SQP values and weights of vial containers

Figure 5 shows the distribution of background counting rates for each vial. The counting band width is the same as that of the ^{14}C measurement for tree rings; the average counting rate is 0.086 cpm/g DB, with a standard deviation of 0.0045. Because the counting statistics show ~1-σ errors (0.0048 cpm/g DB) for these measurements, the count rate fluctuation of each vial is a statistical relation. The small error range indicates that there are no vials with serious radioactive impurities for any of the lots.

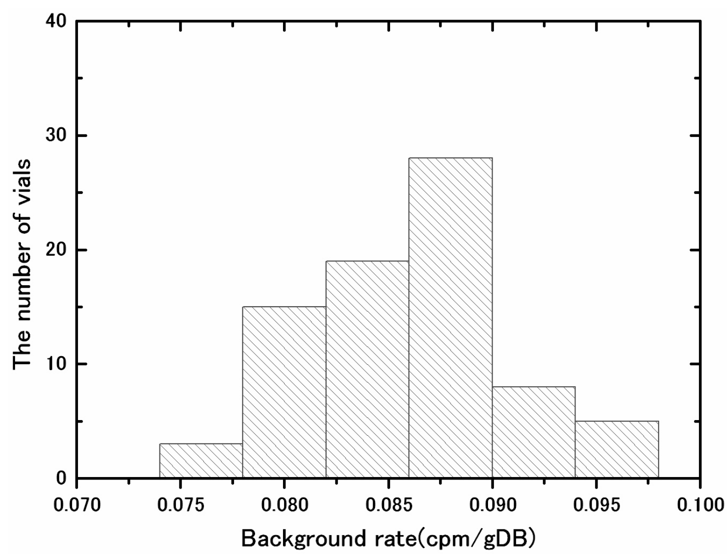

Figure 5 Distribution of background rate by DB for vials

Normalizing Method for Counting

Although the SQP values ranged from 881 to 897 channels for 78 vials, about 85% of the vials were between 888 and 896 channels (see Figure 3). The SQP values of the total benzene (TB) produced from tree rings indicate a good correlation with that of DB, with SQP values ~3 channels lower than for TB, ensuring that the SQP value for DB can be used for selecting vials.

Even if each TB is produced with the same SQP, the spread of SQP values for each vial is a serious problem when determining accurate counts from the pulse-height spectrum (PHS) of ^{14}C. However, since the difference in light yield in Quantulus is indicated with an offset of channels in the PHS, we can estimate the offset as a shift in the channel of the PHS from a reference spectrum (Suzuki et al. 1999; Endo et al. 2000). As the concentration of ^{14}C for TB is determined relative to standard benzene (SB) produced from oxalic acid by NIST, the PHS of SB is the reference spectrum. Thus, if the PHS of TB has an offset compared to SB, we can normalize the ^{14}C concentration of TB to that of SB by using the shift channel between both the PHS values, which is calculated by a least-squares-fitting method.

To ensure that the normalization method is valid, 3 vials with different SQP values were chosen for DB measurements, and ~30 g of the equal-quality benzene (CB) produced from manufactured cellulose is divided into vials A, B, and C. Figure 6 shows each PHS for 3 vial types and the PHS of SB, and the differences in their light yield. Table 2 gives the SQP values of DB and CB and the shift and start channels compared with those of NIST for SB.

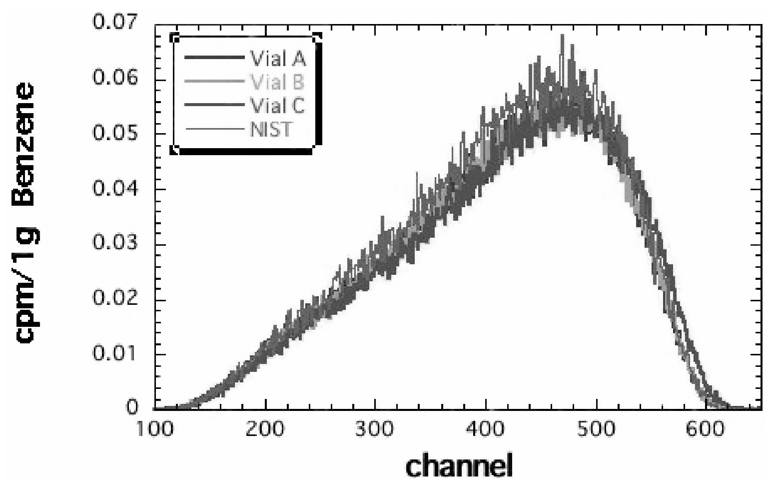

Figure 6 Pulse-height spectra of the vials A, B, and C for equal-quality benzene (CB), and of NIST for standard benzene (SB).

Table 2 Spectral quench parameter (SQP) values for vials A, B, and C and their shift and start channels compared with those of NIST for standard benzene (SB). DB = dead benzene; CB = equal-quality benzene.

Sample	SQP for DB (channel)	SQP for CB (channel)	Shift channel	Start channel
Vial A	897.33	890.21	0	180
Vial B	897.58	891.14	0	180
Vial C	903.5	897.66	10	190
NIST	891.02	889.58 (SB)	0	180

Although the SQP values for CB are ~7 channels lower than for DB, the difference in the SQP value for each vial is approximately the same for both DB and CB. This implies that when the qualities of each benzene sample are similar, the difference in SQP values may be caused by the difference in the light yield of the vials. Although the difference in the SQP value between vials A and C was 7.45, the shift was 10 channels at the start channel of 190.

Figure 7 shows the ratio of count rates per 1 g benzene of CB to the SB for vials A, B and C; we denote this ratio as *K*. Before normalization, the *K* values for vials A, B, and C are 0.9129, 0.9101, and 0.9167, respectively. After normalization, the *K* values are 0.9133, 0.9109, and 0.9130 (0.0031 error). Naturally, the *K* for vials A, B, and C should be the same within the statistical error because the quality of CB is exactly the same. The *K* of vial C after normalization was within 0.1% of the average *K* of vials A and B, although the *K* before normalization was 0.6% on average. These results indicate that the normalizing method is effective in obtaining accurate ^{14}C concentrations of tree rings.

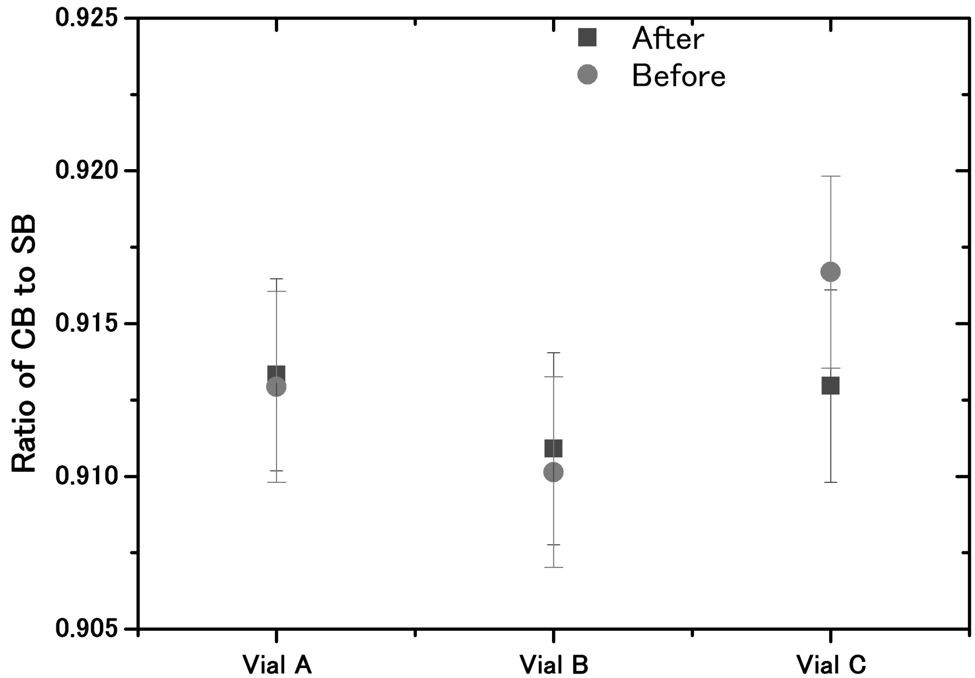

Figure 7 *K* values for vials A, B, and C before and after normalization

CONCLUSIONS

The ^{14}C concentration of ~2500-yr-old tree rings was measured at single-year intervals to investigate the 11-yr periodicity of solar activity. Measurements were carried out on a large amount of benzene (10 g) produced from the tree rings using the ultra low-level LSC system Quantulus, with an accuracy of 0.2%. Since it is important to prepare many vials of the same quality with high light yields for accurate ^{14}C measurements, 78 high-purity Teflon copper counting vials (20 mL) were investigated for weight, light yield, and background counting rate.

The relative standard deviations of the container weights and the copper cap weights are 1.7% and 0.75%, respectively, implying that slight differences in production may cause the Teflon containers' weight to vary as much double the copper cap weight differences. The light yields of the vials investigated with SQP values using DB indicate a small positive correlation between the SQP values and the container weights. From this trend, we infer that the Teflon material influences the diffusion of scintillation light and hence causes a small increase in light yield. The average background counting rate is 0.086 cpm/g DB with a standard deviation of 0.0045 for all vials, indicating that there are no vials with serious radioactive impurities for any lots.

If the pulse-height spectrum of TB has an offset to that of SB, using the shift channel between both PHS values (calculated by a least-squares-fitting method) will cause the ^{14}C concentration of TB to be normalized to that of SB. The validity of the normalizing method was ensured using 3 vial types with different SQP values and approximately 30 g of the equal-quality benzene (CB).

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