A SECONDARY STANDARD FOR RADIOCARBON DATING *

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ABSTRACT. The preparation and calibration of a secondary stand-
ard for the INGEIS Radiocarbon Dating Laboratory are presented.
This standard is barium carbonate with a specific activity al-
most twice that of NBS oxalic acid. It was prepared from $BaCO_3$
with high specific activity and commercial potassium carbonate
by an isotopic dilution technique. The advantages of this stand-
ard are: 1) the preparation is simple and can be achieved with
ordinary labware; 2) the production of CO_2 by acid attack from
this carbonate shows minimum isotopic fractionation. At least,
it has less fractionation than wet oxidation of oxalic acid,
the problems of which are described in the literature. This
standard ensures better reproducibility in activity measure-
ments; 3) despite some problems of activity exchange with at-
mospheric CO_2 concerning carbonates, measurements of activity
over a period of about two years have shown no significant de-
viation from the mean value. A tentative explanation of this
phenomenon is also given. The activity ratio between $BaCO_3$ and
NBS oxalic acid is given with its error, and the statistical
tests used in the calibration are briefly explained. Finally, a
control chart for the activity of the standard over a long pe-
riod is drawn, showing non-significant deviation and support-
ing the usefulness of this standard.

INTRODUCTION

Because NBS oxalic acid standard for ^{14}C dating is avail-
able only in limited quantities, we saw the need for a ^{14}C-la-
beled substance that could be used as a secondary standard.
This substance should show stability and reproducibility in ac-
tivity measurements, it should be easily obtained, and its spe-
cific activity should be similar to that of modern ^{14}C activity.
Our ^{14}C laboratory has been operating since 1979 using
benzene synthesis and liquid scintillation counting techniques
(Tamers, 1975) and dates ca 200 archeologic and geologic sam-
ples per year.
The criteria that the standard should achieve are: 1) The
activity must be similar to that of NBS oxalic acid. If speci-
fic activity is too high, it could cause contamination in the
synthesis line. Low specific activity would increase the count-
ing times. A specific activity about twice that of NBS was

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chosen. 2) Easy preparation-the standard should be synthesized with ordinary labware and easily converted to benzene. It could be processed as any sample; 3) It should not show isotopic fractionation, a problem with NBS oxalic acid (Grey et al, 1969), which shows appreciable fractionation in derived CO_2. This is because the reaction of oxalic acid with a sulfuric solution of potassium permanganate is a redox reaction of slow kinetics. We wanted a carbonate because the reaction with acid to obtain CO_2 is one of quick kinetics, so that it should show no isotopic fractionation; 4) Homogeneity of the standard-synthesis of the standard should ensure that the product is homogeneous which is important for the reproducibility of its activity.

PREPARATION OF THE STANDARD

From ^{14}C labeled barium carbonate of high specific activity (ca 88000dpm/g), an isotopic dilution was performed as follows: The labeled barium carbonate was dissolved with concentrated phosphoric acid under vacuum and the CO_2 was absorbed in a potassium hydroxide solution. This solution was mixed with a saturated solution of commercial potassium carbonate. The dilution of the specific activity and the homogeneity was achieved by gently stirring. A warm solution of barium chloride is neutralized because the hydrolysis of Ba^{2+} gives a pH of ca 4.5 and the carbonate precipitated would redissolve at this pH; then it is mixed with the former carbonate solution. The barium carbonate is precipitated with a crystal size suitable for filtering. The precipitate is then washed and dried at ca 110°C.

We observed that potassium chloride was coprecipitated with the barium carbonate as a result of reacting with saturated solutions; this potassium chloride does not affect the usefulness of the standard. Ca 2200g of the standard were obtained from 45 mg of high specific activity barium carbonate. This quantity will be enough for about two years' work.

CALIBRATION OF THE STANDARD

MEAN VALUE OF $\delta^{13}C$. In order to check the hypotesis that this standard should not show problems of isotopic fractionation, the $\delta^{13}C$ value was determined for seven samples with the following results (table 1):

TABLE 1. $\delta^{13}C$ values of the secondary standard

Sample no.	1	2	3	4	5	6	7
$\delta^{13}C$ (‰)	-26.4 ± .4	-26.5 ± .4	-27.1 ± .6	-26.1 ± .6	-26.5 ± .4	-26.4 ± .5	-26.4 ± .6

Mean value = -26.5‰ ; Standard deviation = 0.3‰

The δ^{13}C measurements were performed in the Stable Iso-
topes Laboratory of INGEIS using a double collector Micromass
602-D mass spectrometer. The small standard deviation shows
that the criteria 3) in the introduction is fulfilled and the
mean value is considered as a reference to correct the activi-
ty of the standard by isotopic fractionation.

ACTIVITY CALIBRATION. Following the technique described by
Tamers (1975), 5 benzene synthesis of the standard and two of
NBS oxalic acid were made. The activity of these samples, to-
gether with background, were measured in a Packard 3255 Liquid
Scintillation Spectrometer. The measured activities of the NBS
oxalic acid were corrected according to Faure, (1977):

$$A_{NBS}^{corr} = (A_{NBS} - A_F) \cdot \left[1 - \frac{2 \cdot (\delta^{13}C_{NBS} + 19.0)}{1000} \right] \quad (1)$$

where A_{NBS}^{corr} = corrected activity of the NBS oxalic acid

A_{NBS} = gross activity of the NBS oxalic acid

A_F = background

$\delta^{13}C_{NBS}$ = measured value of NBS oxalic acid δ^{13}C
vs PDB

Similarly the activity of the standard was corrected using
the following equation:

$$A_P^{corr} = (A_P - A_F) \cdot \left[1 - \frac{2 \cdot (\delta^{13}C_P + 26.5)}{1000} \right] \quad (2)$$

where A_P^{corr} = corrected activity of the standard

A_P = gross activity of the standard

$\delta^{13}C_P$ = measured value of δ^{13}C of the standard
vs PDB

The activity measurements of the standard and the NBS
oxalic acid are shown in tables 2 and 3.

TABLE 2. Activity measurements of NBS oxalic acid

NBS	A_{NBS} (cpm)	A_F (cpm)	$\delta^{13}C_{NBS}$ (‰)	A_{NBS}^{corr} (cpm)	Counting time(min)
1	56.02±.20	9.65±.08	−20.3±.5	46.50±.22	1380
2	57.23±.22	10.80±.09	−18.2±.2	46.36±.24	1220

TABLE 3. Activity measurements of the secondary standard

Secondary standard	A_P (cpm)	A_F (cpm)	$\delta^{13}C_P$ (‰)	A_P^{corr} (cpm)	Counting time(min
1	109.88±.27	10.06±.08	−26.4±.4	99.80±.28	1480
2	110.22±.27	10.06±.08	−26.4±.4	100.17±.28	1480
3	109.94±.33	9.64±.08	−26.4±.4	100.29±.34	1000
4	109.15±.33	9.64±.08	−26.5±.4	99.52±.34	980
5	110.96±.30	10.80±.09	−26.2±.6	100.10±.31	1200

Samples of 5ml of benzene corresponding to the standard and NBS oxalic acid were measured in different runs. Counting time was divided in periods of twenty minutes, allowing statistical treatment of the data. Using Chauvenet's criterion, we rejected data that deviated significantly from the mean. For NBS oxalic acid samples, the net corrected activities were compared by means of the statistic "t" (Student) for a confidence of 95%, with no significant difference between the two corrected activity values. We were able to obtain a mean value of:

$$A_{NBS\ mean}^{corr} = (46.47\pm.15)cpm$$

For the standard, we had to stablish whether differences in measurements were due to statistical or systematic errors. If the former, the standard would be isotopically homogeneous. This can be determined by an analysis of variance (ANOVA) of the five sets of activity values (20-minute measurement each) corresponding to the standard samples. First we had to determine that the five sets showed quality of variances by using statistic "F" (for a confidence of 95%). The results of the ANOVA showed that the differences between the mean value of each set (table 3) was due only to the statistical deviation of radioactivity (Poisson) and not to systematic errors. Thus, the homogeneity of the standard was also proven. We were then able to obtain a mean value for the standard activity:

$$A_{P\ mean}^{corr} = (99.98\pm.15)cpm$$

The activity factor between the secondary standard and the NBS oxalic acid and its error were then calculated:

$$\gamma = \frac{A_{NBS\ mean}^{corr}}{A_{P\ mean}^{corr}} = .4648 \qquad \sigma_\gamma = .0016 \qquad (3)$$

STATISTICAL CONTROL OF THE STANDARD

Each time a new series of samples to be dated is measured, the net corrected activity of the standard is controlled by means of a "t" test (95% confidence), using the value of 99.98 cpm as a reference value:

$$t_{.95,\ n-1} = \frac{\overline{X} - \mu}{S/\sqrt{n}} \qquad (4)$$

where $\overline{X}$ = net corrected activity of the measured standard.

S = standard deviation

n = number of cycles of measurement

μ = 99.98cpm

The result of 14 measurements are presented in table 4, and plotted vs time in figure 1. The areas of ±1σ and ±2σ levels of confidence are also drawn in figure 1.

TABLE 4. Results of measurements made with the secondary standard.

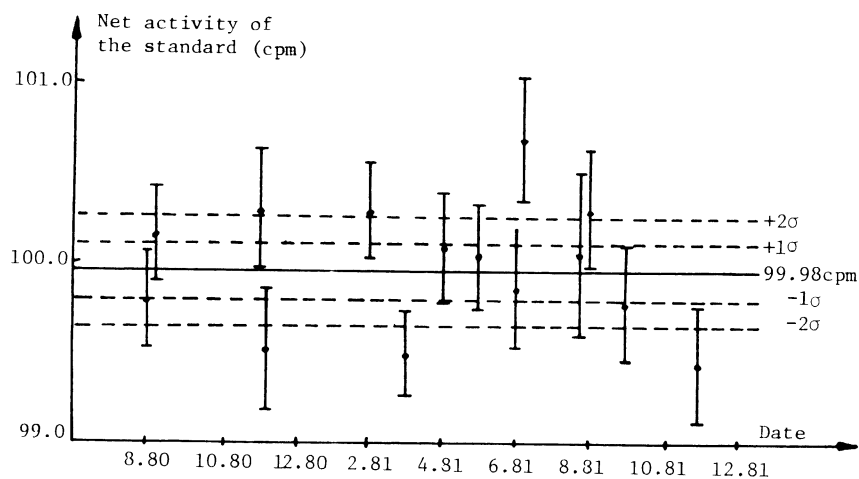| Month/ year	A_P^{corr} (cpm)	$\delta^{13}C$ (‰)	no. of 20 min counts	t(Student)
8/80	99.80+.28	−26.4+.7	74	−.64
8/80	100.17+.28	−27.1+.6	74	.68
11/80	100.29+.34	−26.4+.4	50	.91
11/80	99.52+.34	−26.1+.5	49	−1.35
2/81	100.29+.27	−26.8+.2	83	1.15
3/81	99.50+.25	−26.8+.2	50	−1.92
4/81	100.10+.31	−26.2+.6	60	.39
5/81	100.05+.29	−26.2+.6	69	.24
6/81	100.68+.35	−26.5+.2	49	2.03
6/81	99.86+.34	−26.2+.6	50	−.35
7/8/81	100.05+.48	−26.5+.3	25	.15
8/81	100.30+.35	−26.1+.3	49	.91
9/81	99.79+.34	−26.1+.3	50	−.56
11/81	99.44+.34	−26.1+.3	50	−1.59

Fig 1. Net activity of the secondary standard vs time

CONCLUSIONS

The secondary standard has achieved the goals set out at the beginning of our project.

The resulting activity is about twice that of the NBS o-xalic acid:

$$A_P = A_{NBS} \cdot (2.1515 \pm .0074)$$

The data show good reproducibility resulting from homogeneous dilution of the initial high specific activity; reproducibility of the whole synthesis and measurement procedures are also shown.

Isotopic fractionation of the standard is negligible, as shown in the $\delta^{13}C$ values of tables 1 and 4.

It has been noted that a ^{14}C exchange occurs between ^{14}C labeled carbonates and atmospheric CO_2 and these carbonates lose activity with time. This is a result of the following exchange reaction:

$$^{14}CO_3^= + CO_2 \xrightleftharpoons{H^+} CO_3^= + {}^{14}CO_2 \tag{5}$$
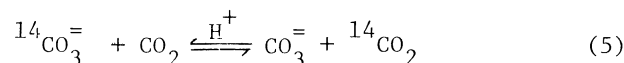
catalized by small quantities of CO_3H_2.

Our secondary standard has not shown this behavior; its specific activity has been constant right along. A tentative explanation is that the rate of the exchange depends on the difference of activity of the carbonate and the CO_2. The exchange has been noticed in carbonates with high specific activity, which is much higher than the natural levels of CO_2. In our case, both activities, atmospheric CO_2 and the standard, are comparable, making the exchange negligible.

ACKNOWLEDGMENTS

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