

# Radiocarbon

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## MEASUREMENT OF THE $^{14}\text{C}$ ACTIVITY OF THE ANU SUCROSE SECONDARY STANDARD BY MEANS OF THE PROPORTIONAL COUNTER TECHNIQUE

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**ABSTRACT.** A systematic crosschecking of the NBS oxalic acid standard, the ANU Sucrose secondary standard, and the RB oak tree rings grown in  $1858 \pm 5$  and  $1890 \pm 5$  has been performed using the proportional counter technique. Details on the counter gas (methane) purification are given. Corrections of count rates due to changes of barometric pressure and ambient temperature are applied and discussed. Results of measurements are presented and the ratios between mean activities of the NBS oxalic, ANU sucrose and RB oak samples are given.

### INTRODUCTION

The prospect of vanishing stock of the NBS oxalic acid which has been used as the reference standard by many radiocarbon laboratories instigated a search for suitable secondary standards whose activity can be correlated with the activity of the NBS oxalic acid standard and/or the primary wood standard. The ANU Sucrose proposed by Polach and Krueger (1972) meets most of requirements for such a secondary standard: sucrose is chemically inert and relatively stable in comparison to inorganic compounds (carbonates); its molecular structure does not favor isotopic exchange in contact with atmospheric  $\text{CO}_2$  during storage in dry form. Handling of samples is easy although combustion is not so straightforward; to compensate for tedious combustion the ANU sucrose gives, according to Polach and Krueger (1972), less spread in isotopic fractionation of the obtained  $\text{CO}_2$ . However, what makes the ANU sucrose a favorite and most attractive secondary standard is the fact that, thanks to efforts of Henry Polach and the Australian sugar and packaging industry, a large amount of high purity sucrose has been carefully stored, ready for free distribution to radiocarbon laboratories around the world. Since the amount of the NBS oxalic standard has become very limited in our laboratory, a decision was made in 1977 to start the cross-calibration of the ANU sucrose secondary standard with the NBS oxalic acid standard.

### *Experimental*

Our routine radiocarbon measuring system is based on combustion of the sample in a stream of purified oxygen, followed by trapping and purification of the  $\text{CO}_2$  and subsequent conversion to  $\text{CH}_4$  by hydrogenation via Ru catalyst. Methane is purified and counted in a propor-

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tional counter in anticoincidence with a ring guard counter. The essential features of the system have been described elsewhere (Srdoč, Breyer, and Sliepčević, 1971). However, several modifications in gas handling, gas purification, and electronics as well as in computer processing of data have been introduced, resulting in higher precision of measurements. Also, the background count has been reduced significantly, thus improving the figure of merit. Modifications and resulting improvements will now be described.

#### *Gas purification technique*

Our gas purification technique has been improved by applying vacuum distillation of the gas mixture obtained by the hydrogenation of  $\text{CO}_2$ . The gas mixture after hydrogenation consists of  $\text{CH}_4$ , water vapor, surplus of hydrogen, unreacted  $\text{CO}_2$  and traces of impurities, mainly CO and higher hydrocarbons. The vacuum distillation proceeds as follows: the bottom of the reaction vessel (fig 1), containing the gas mixture after catalytic hydrogenation, is kept at liquid  $\text{N}_2$  temperature. All gases except  $\text{H}_2$  are thus condensed;  $\text{H}_2$  is then pumped off for a short time; prolonged pumping would result in loss of  $\text{CH}_4$  due to its relatively high vapor pressure at liquid  $\text{N}_2$  temperature. Liquid  $\text{N}_2$  is then replaced by dry ice+alcohol mixture. Water and heavy hydrocarbons are thus kept frozen and the rest of the gas mixture containing  $\text{CH}_4$ , traces of  $\text{CO}_2$ , and CO is condensed in a stainless steel container kept at liquid  $\text{N}_2$  temperature (A in fig 2). Final distillation is performed by connecting container A with the  $\text{CH}_4$  and traces of impurities kept at liquid  $\text{N}_2$  temperature to the stainless steel container, B, filled with silicagel and also kept at liquid  $\text{N}_2$  temperature. A slow distillation of  $\text{CH}_4$  follows since the pressure of  $\text{CH}_4$  above silicagel is much lower. Traces of  $\text{CO}_2$ , CO,  $\text{C}_2\text{H}_4$ , and  $\text{C}_n\text{H}_{2n+2}$  remain frozen at liquid  $\text{N}_2$  temperature in the container A (fig 2). Their vapor pressure is so low at liquid  $\text{N}_2$  temperature that they practically remain trapped in container A. The  $\text{CH}_4$  obtained by the described vacuum distillation is practically free of any impurity which would exceed 10 to 100 ppm, as shown by gas chromatographic and mass spectrometric analyses. However, the gas multiplication factor, defined as the mean number of electrons formed in the single electron avalanche, is sensitive at high gas pressure even to such small amounts of impurities ranging from 10 to 100ppm when oxygen or any other electronegative gas is in question. Any change of the gas multiplication factor shifts the mean counting rate of the sample, causing an error in sample activity measurement. This was proved by measuring the counter resolution using the  $^{55}\text{Fe}$  source. The counter resolution, expressed as the full width at half maximum (FWHM) of the measured spectrum, divided by the source energy, is a sensitive index of the counter performance, routinely used in nuclear spectroscopy. Broadening of spectrum and decreasing of gas multiplication were observed whenever methane was contaminated with air. The described vacuum distillation failed to restore the gas purity existing

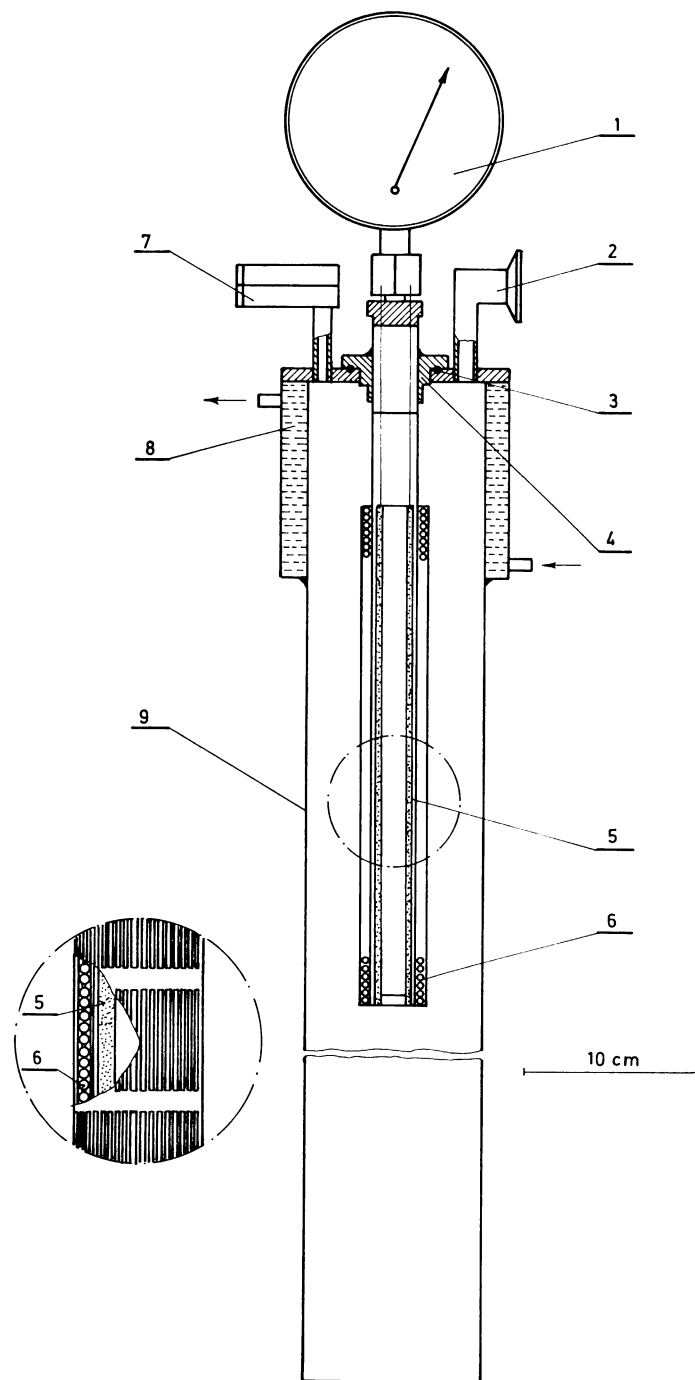


Fig 1. The methane converter. 1—pressure gauge; 2—vacuum pump flange; 3—Viton O-ring; 4—catalyst holder; 5—heater; 6—catalyst; 7— $\text{H}_2$  and  $\text{CO}_2$  inlet valve; 8—cooling coil; 9—stainless steel tank.

prior to contamination. Therefore, another step of gas purification follows the vacuum distillation. The next step of gas purification consists of passing methane through red hot copper turnings and a column filled with Anhydron and Ascarite. No thermal decomposition of methane has been observed at the working temperatures of 650°C. Copper at elevated temperatures removes, effectively, any trace of oxygen. It remains bright after prolonged use, being constantly flushed with methane. Anhydron and Ascarite remove water vapor and CO<sub>2</sub>, respectively. High purity methane, thus obtained, has excellent counting properties; the resolution of the proportional counter filled up to 3 atm with purified gas is ≈16.5 percent for <sup>55</sup>Fe source.

Routine testing of gas purity is performed by measuring the counting rate in the middle of the initial steep part of the plateau curve. A 1 mCi <sup>226</sup>Ra source is carefully positioned in a fixed place close to the counter, providing a constant exposure rate. The counting rate at the chosen steep part of the plateau is extremely sensitive to gas contamination; this simple method replaces pulse height analysis which requires expensive electronics. Any gas sample that does not reach an empirically determined counting rate when exposed to the fixed dose rate at the selected voltage is subjected to the repeated purification.

#### *Counting procedure and computer processing of data*

Because of frequent disturbances in the power network as well as electronic failures, it was necessary to divide the measurement of sample activity into 20min intervals. Thus, long lasting measurements are not lost if a failure occurs. Besides, the statistical processing of data enables

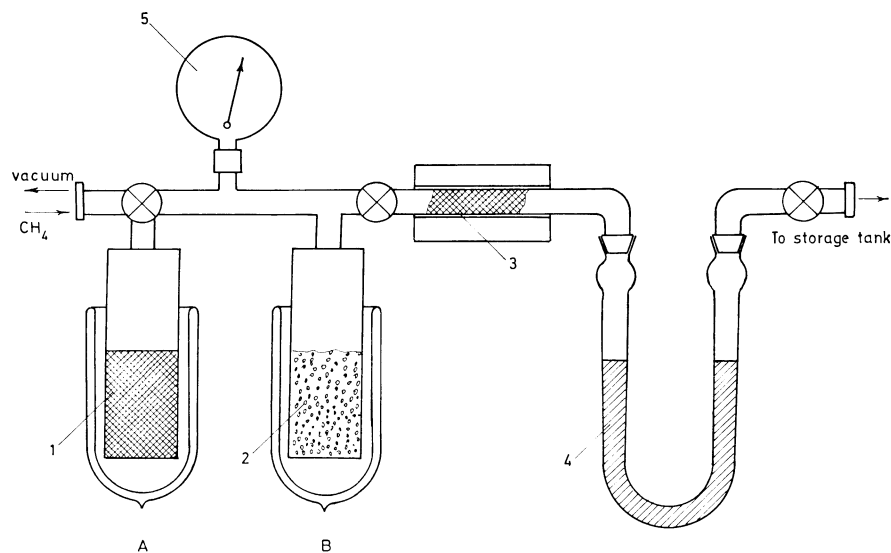


Fig 2. The methane purifier. 1—Cu turnings; 2—Silicagel; 3—Cu turnings; 4—Anhydron-Ascarite filling; 5—pressure gauge.

the rejection of data that do not fit into statistical distribution (Chauvenet's criterion). Analysis of data printed on a strip chart revealed two effects that influenced the measurement: 1) the barometric effect, and 2) changing of the gas multiplication factor. A reciprocal correlation was found between the background count rate and the barometric pressure.

The mean coefficient  $A = \overline{\Delta B}/\Delta P$  has been evaluated from experimental data. Averaged over a year, the mean coefficient,  $A$ , can be expressed as follows:

$$A = \frac{\overline{\Delta B}}{\Delta P} = \frac{\overline{B} - B}{\overline{P} - P} = -0.0136 \text{ CPM/Torr} \quad (1)$$

where  $\overline{B}$  is the mean background counting rate at the mean yearly barometric pressure  $\overline{P}$ , which is equal to 748 Torr in our case.  $B$  and  $P$  correspond to sample background count and the mean barometric pressure during the measurement, respectively. The relative mean change of the background count rate is equal to  $-0.0024\text{CPM}$  per torr, at the present background count rate of  $5.65\text{CPM}$ . Rearranging eq 1,

$$\overline{B} = B + A\Delta P \quad (2)$$

is obtained.

The background count rate does not depend very much on small variations of gas pressure inside the counter. On the contrary, sample count rate depends on the total amount of gas in the counter; hence, eq 3 takes into account the difference between the filling temperature and the reference temperature ( $18^\circ\text{C}$ ) and the barometric effect:

$$\begin{aligned} S - \overline{B} &= [S(P,T) - B(P)] T/T_r \\ S - \overline{B} &= [S(P,T) - (\overline{B} - A\Delta P)] T/T_r \end{aligned} \quad (3)$$

$S$  denotes the sample gross count rate reduced to the mean barometric pressure and the reference temperature.  $S(P,T)$  is the actual sample gross count rate at the barometric pressure,  $P$ , and temperature,  $T^\circ\text{K}$ .  $T_r$  is the reference temperature, and  $T$  is the actual temperature at the moment of filling of the counter. Sample, standard, and background activities presented in section 3, have been calculated by using eq 3.

Although eq 3 helps correct the data, the correlation coefficient has been relatively low; this means that the standard deviation of the coefficient,  $\overline{\Delta B}/\Delta P$ , is large, and consequently, the correction for the change of barometric pressure is not perfect. Obviously, the barometric pressure is not the only parameter that influences the background counting rate.

The changing gas multiplication factor is caused by increasing contamination of the counter gas during the storage and counting period. The main source of gas contamination is outgassing of containers, gas lines and the counter, and air leakage or diffusion of air through gaskets, o-rings, et cetera. Deterioration of gas counting properties was also observed in the course of counting. Changing of the gas multiplication fac-

tor during gas storage has been suppressed by filling the gas containers with silicagel, which acted as a purifier probably absorbing polyatomic contaminants and accelerating elimination of free oxygen in the highly reducing atmosphere. Deterioration of gas during the counting cannot be completely eliminated. It could be diminished, though, by keeping the gas lines and the counter under the working pressure of methane all the time, strictly preventing exposure to air. The counting time should be comparable for background, standard, and sample measurement. A small correction of counting rate (0.06 percent per hour over 48<sup>h</sup>) has been applied, based on the experimentally observed drop of counting rate for prolonged measurement, by extrapolating to the "standard" 48hr measurement. Computer processing of data greatly facilitates calculation of corrections, statistical evaluation of data, and final calculation of  $\Delta^{14}\text{C}$ , percent modern, and the age of a sample. Details of computer processing are presented elsewhere (Obelić and Planinić, 1975).

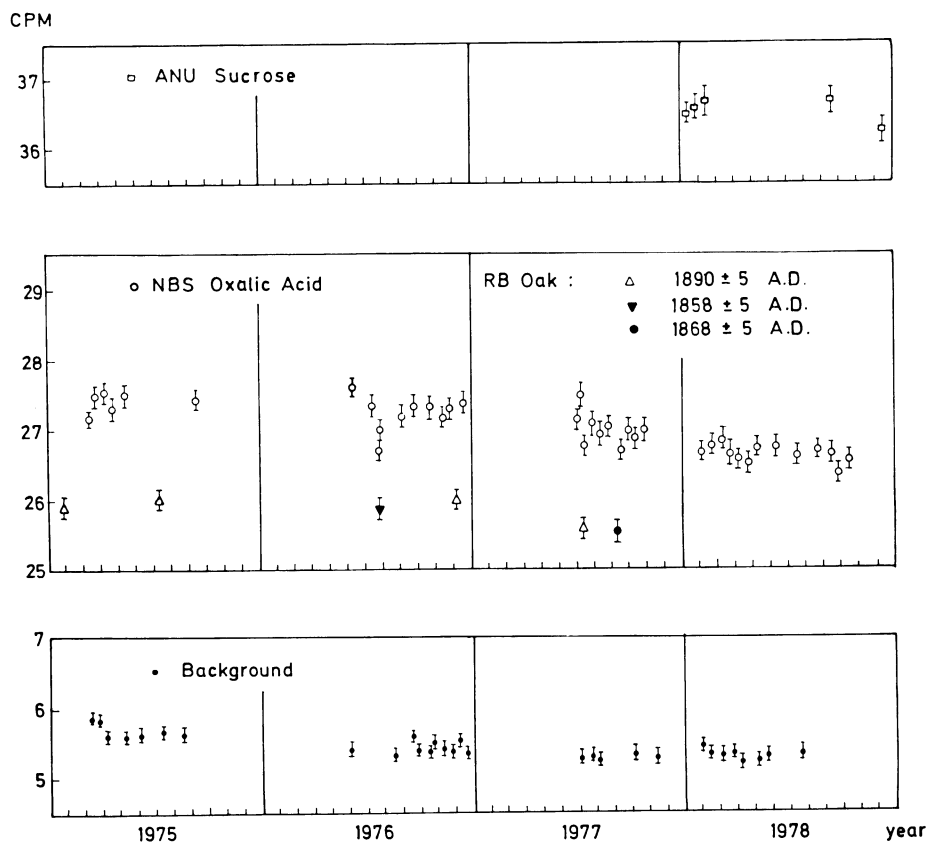


Fig 3. Measurement of activity of the NBS oxalic acid, the ANU sucrose, the RB oak tree rings, and the background.

## RESULTS

*Experimental data*

The results of measurement of the NBS oxalic acid standard, ANU sucrose, RB oak tree rings grown in years 1858 and 1890, and the background count rate are presented in figure 3.

Counting rates of the NBS oxalic and the background varied slightly in the period 1975 to 1979 due to minor adjustments of electronic and gas gains. Therefore, measurements of standard and background activities are grouped and mean values calculated for each set of data. These values are used appropriately for measurements of samples in 1975 through 1978.

Wood samples were prepared from an oak tree grown on site, Rudjer Bošković Inst ( $45^\circ 49' \text{ N}$ ,  $15^\circ 59' \text{ E}$ ) 180m above MSL, felled in 1973. Tree rings were counted at the Faculty of Forestry, Univ Zagreb. Ten tree rings corresponding to years  $1858 \pm 5$ ,  $1868 \pm 5$ , and  $1890 \pm 5$  were cut from a large wood disk. Wood samples were treated with 4 percent HCl and 4 percent NaOH as described (Srdoč, Breyer, and Sliepevic, 1971, p 135).

*Calculation of ratios*

Using the weighted mean values from figure 3, the following ratios were obtained between the activity of various samples, corrected for isotopic fractionation:

$$\frac{\text{Net ANU Sucrose CPM}}{\text{Net NBS Oxalic acid} \times 0.95} = 1.5012 \pm 0.0032$$

The  $\delta^{13}\text{C}$  ratios of NBS oxalic acid and the ANU sucrose samples prepared at our laboratory were measured by H Polach, ANU, Canberra, Australia and gave the following values:

$$\text{NBS oxalic acid } \delta^{13}\text{C}: -18.6 \pm 0.4$$

$$\text{ANU sucrose } \delta^{13}\text{C}: -11.4 \pm 0.4$$

The ratio between the  $^{14}\text{C}$  activity of the oak wood tree rings grown nominally in 1858, 1868, and 1890, converted to year 1950 and the activity of the NBS oxalic also corrected for decay is presented in table 1. The activities are corrected for isotopic fractionation (Ox  $\delta^{13}\text{C} = -19\text{‰}$ , wood  $\delta^{13}\text{C} = -24\text{‰}$ ). The mean ratio  $A_{\text{wood}}/A_{\text{ox}}$  shown in table 1 for samples of wood grown before industrial era (Suess effect) and nuclear weapon tests is  $0.949 \pm 0.004$  which is in agreement with the accepted value, 0.95.

TABLE 1

$$\frac{A_{\text{wood (1858} \pm 5 \text{ yr)}}}{A_{\text{NBS oxalic}}} = 0.955 \pm 0.008$$

$$\frac{A_{\text{wood (1868} \pm 5 \text{ yr)}}}{A_{\text{NBS oxalic}}} = 0.944 \pm 0.004$$

$$\frac{A_{\text{wood (1890} \pm 5 \text{ yr)}}}{A_{\text{NBS oxalic}}} = 0.949 \pm 0.004$$

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