

ISOTOPIC FRACTIONATION OF NBS OXALIC ¹⁴C STANDARD AND ITS EFFECT ON CALCULATED AGE OF MATERIALS

VICTOR A NEHMI

Centro de Pesquisas Geocronológicas, Instituto de Geociências,
Universidade de São Paulo, 05508 São Paulo, Brazil

ABSTRACT. There is much controversy about the significance to radiocarbon dating of isotopic fractionation during the oxidation to CO₂ of NBS oxalic acid, the carbon-14 dating standard. To check the effect of fractionation, 30 routine potassium permanganate oxidations of oxalic acid were performed. The isotopic composition of resulting CO₂ was determined mass-spectrometrically. δ¹³C results ranged between -17.7 and -21.2, with an average of -18.9‰ wrt PDB. The effect of not applying an isotopic fractionation correction to NBS oxalic acid when performing age calculations is evaluated.

INTRODUCTION

Oxalic acid, distributed by the National Bureau of Standards, Washington, DC, is used as a contemporary standard for radiocarbon dating. Two methods of oxidation to CO₂ are generally practiced: 'dry combustion' and 'wet oxidation'. The latter uses acidified potassium permanganate (KMnO₄) and appears to be used more commonly but with varying degrees of success. Kim (1970) and Valastro, Land, and Varela (1977), for example, demonstrate that with reasonable care no or little carbon-isotopic fractionation occurs. Others (eg, Grey and others, 1969; Polach and Krueger, 1972) demonstrate that severe isotopic fractionation can be induced and conclude that great care in oxalic standard preparation is required to avoid adverse isotopic effects. This paper looks at some 30 'wet oxidation' reactions, performed routinely, albeit with care, and analyzes the variability of δ¹³C (*ie*, mass-spectrometrically measured ¹³C/¹²C ratio) and their effects on radiocarbon age determinations.

Isotopic fractionation

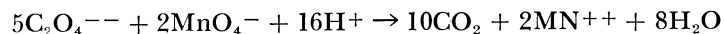
Mass-spectrometric determinations of carbon isotopic abundances of NBS oxalic acid were first carried out by Craig (1961) using the Peedee Formation Belemnite (PDB) as a standard. Based on interlaboratory checks, involving both 'wet' and 'dry' oxidation techniques, he suggested that a standard value, δ¹³C NBS Ox = -19.0‰ wrt PDB, be used by all laboratories. For radiocarbon dating purposes, Stuiver and Polach (1977) recommend that normalization be carried out according to:

$$A_{ON} = 0.95A_{Ox} \left(1 - \frac{2(19 + \delta^{13}C)}{1000} \right)$$

where A_{Ox} is the measured net oxalic activity (count rate) at time of measurement, and δ¹³C = measured ¹³C/¹²C ratio of NBS oxalic wrt PDB in parts per thousand.

EXPERIMENTAL RESULTS AND CONCLUSIONS

Thirty 'wet' oxidations of oxalic acid with potassium permanganate and sulphuric acid (fig 1) have been made according to the reaction:



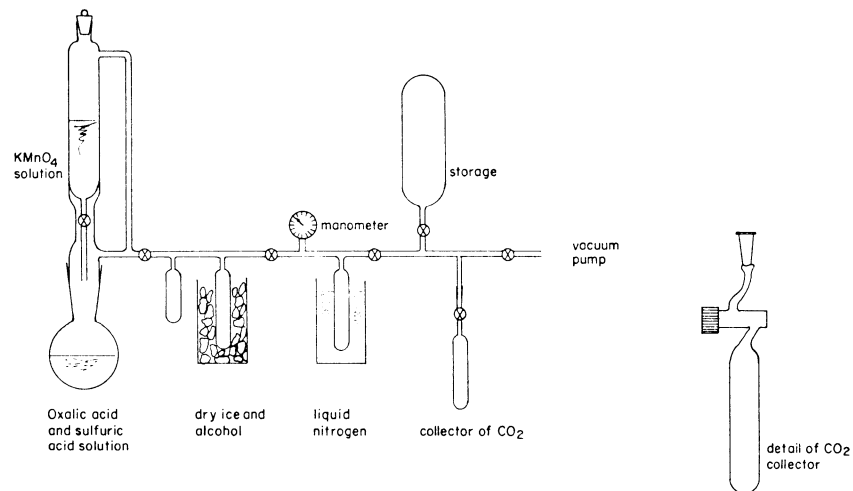
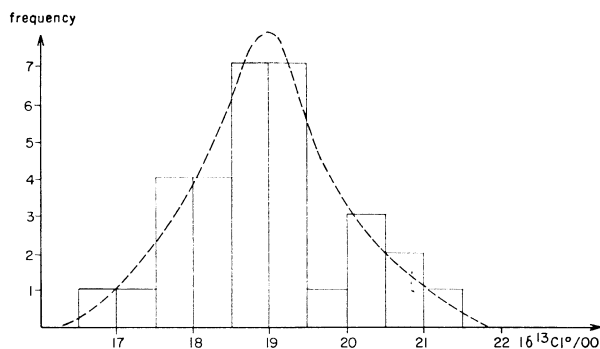


Fig. 1 - LINE OF OXIDATION OF OXALIC ACID WITH POTASSIUM PERMANGANATE

TABLE 1
 $\delta^{13}\text{C}$ values of NBS oxalic acid; oxidation with potassium permanganate

Sample	$\delta^{13}\text{C}$ (‰)	(%)
1	-20.2	96
2	-17.7	94
3	-18.9	96
4	-20.8	92
5	-21.2	98
6	-20.3	90
7	-18.2	92
8	-17.9	92
9	-17.9	92
10	-19.3	96
11	-19.1	90
12	-20.1	94
13	-19.4	96
14	-18.3	96
15	-18.6	96
16	-16.6	94
17	-19.9	92
18	-18.7	90
19	-19.0	90
20	-21.0	92
21	-18.6	90
22	-19.2	90
23	-19.6	98
24	-18.8	96
25	-18.4	92
26	-18.7	98
27	-19.1	96
28	-17.1	96
29	-17.9	92
30	-18.0	96

Fig. 2 - HISTOGRAM OF $\delta^{13}\text{C}$ OF NBS OXALIC ACID

We used 2g of NBS oxalic acid for each preparation. Yields were determined by measuring pressure CO_2 in a standard volume. Table 1 gives the $\delta^{13}\text{C}$ results and individual reaction yields. The average $\delta^{13}\text{C}$ value, at $-18.95 \pm 0.2\text{‰}$ is in excellent agreement with that postulated by Craig and other workers. The standard deviation of all $\delta^{13}\text{C}$ values is also small (1.1‰), and the distribution of the values around their mean is normal (fig 2).

The $\delta^{13}\text{C}$ value furthest from mean is -21.2‰ . The effect such a deviation would have on ^{14}C ages has been evaluated and is given in table 2. The calculations are based on age determinations of archaeological material dated by the Radiocarbon Laboratory of the Universidade de São Paulo. Table 2 gives both the $\delta^{13}\text{C}$ corrected and uncorrected ages. The error, ca 35 years, when a correction for fractionation of oxalic acid from $\delta^{13}\text{C} = -21.2$ to the base of -19.0 is not applied, is constant throughout the age range. Clearly, isotopic fractionation of NBS oxalic acid must not be ignored, particularly for samples with ages close to modern (young ages).

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TABLE 2
Corrected ages of materials dated at the radiocarbon
laboratory of Universidade de São Paulo

Materials	Non-corrected ages (yr)	Corrected ages (yr)	Deviation (%)
SPC-41	1150	1195	4
SPC-47	2550	2590	1.6
SPC-20	4260	4300	0.9
SPC-6	7950	7990	0.5
SPC-131	15,730	15,780	0.3
SPC-43	28,050	28,080	0.1

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