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INFLUENCE IN THE CALCULATED AGE OF MATERIALS

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ABSTRACT

Much controversy exists about isotopic fractionation during oxidation of NBS oxalic acid to carbon dioxide. To check the intensity of this fractionation, 30 reactions of oxidation of NBS oxalic acid with potassium permanganate were made. The resultant isotopic composition of CO<sub>2</sub> has been determined with a mass-spectrometer. A conclusion has been reached that the average value of  $\delta^{13}\text{C}$  is - 18.9‰ with variation between - 17.7 and - 21.2‰. For values of  $\delta^{13}\text{C}$  equal to - 22.0‰, the calculated age with isotopic correction shows the following deviations in relation to non-corrected age: 4% for materials of 1,000 years and 0.3% for 20,000 years.

## INTRODUCTION

The oxidation of NBS oxalic acid to carbon dioxide with potassium permanganate and sulfuric acid is practised at the radiocarbon dating laboratories, which use a liquid scintillation counter. This reaction, under certain conditions, shows isotopic fractionation. Because NBS oxalic acid is the radiocarbon dating modern reference standard, researchers have discussed the intensity of this isotopic fractionation. Some researchers (e.g. Polach and Krueger, 1972) state that this isotopic fractionation can be high, while others, like Kim (1970) and Lowdon (1969), state that it is small, provided that the reaction be total and carried out with care, that is, yield of the reaction is stoichiometric.

The main method of determining this isotopic fractionation is measure the isotopic relation  $\delta^{13}\text{C}$  of carbon dioxide, through mass-spectrometry.

Craig (1961) suggested that the  $\delta^{13}\text{C}$  of NBS oxalic acid of - 19.0‰ in relation to PDB should be accepted as the normalization value. If the  $\delta^{13}\text{C}$  carbon dioxide, resulting from NBS oxalic acid, is different from this value, the normalization to - 19.0‰ must be done.

To normalize it, Stuiver and Polach (1977) propose the formula:

$$\Delta^{14}\text{C}_{\text{ON}} = 0.95 \delta^{14}\text{C} \left[ 1 - \frac{2(19 + \delta^{13}\text{C})}{1000} \right]$$

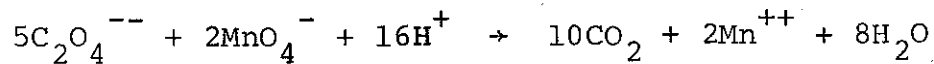
where:

- $\delta^{13}\text{C}$ : carbon 13 isotopic relation of NBS oxalic acid, in relation to PDB;
- $2\delta^{13}\text{C}$ : carbon 14 isotopic relation of oxalic acid, according to Craig's simplification;

- $\delta^{14}\text{C}$ : oxalic acid activity;
- 19.0‰: conventional value of  $\delta^{13}\text{C}$  to oxalic acid;
- $\Delta^{14}\text{C}_{\text{ON}}$ : normalized value of carbon 14 isotopic relation of NBS oxalic acid (normalized activity).

#### MEASURES OF NBS OXALIC ACID ISOTOPIC FRACTIONATION

Thirty total reactions of oxalic acid oxidation with potassium permanganate and sulfuric acid were made according to the equation:



The reaction was undertaken in the radiocarbon laboratory. Two grams of NBS oxalic acid were used in each reaction and the yields of the reactions were determined through carbon dioxide pressure, read at the manometer. Table 1 shows the 30 values of  $\delta^{13}\text{C}$  and its respective yields.

The average of this 30 values of  $\delta^{13}\text{C}$  is - 18.9‰. This value coincides with the value obtained by Lowdon (1969), but it differs from the value - 20.2‰, obtained by Polach et al (1972). Figure 2 gives the histogram of the  $\delta^{13}\text{C}$ . The standard deviation of these values is 1.1‰.

#### INFLUENCE ON THE CALCULATED AGE

Among the 30 values  $\delta^{13}\text{C}$ , the one farthest from - 19‰ is - 22.0‰. This value causes, therefore, a greater deviation in the calculated age of materials with isotopic fractionation. The calculated age was obtained through the

formula:

$$t = 8033 \ln \frac{\Delta^{14}C_{ON}}{\Delta^{14}C_{MN}}$$

where:

$\Delta^{14}C_{ON}$ : normalized activity of NBS oxalic acid, to - 19.0‰;

$\Delta^{14}C_{MN}$ : normalized activity of materials, to - 25.0‰.

Table 2 shows corrected ages of some materials dated at the radiocarbon laboratory of the Universidade de São Paulo.

#### CONCLUSION

Isotopic fractionation of NBS oxalic acid, in its oxidation to carbon dioxide with potassium permanganate and sulfuric acid, is small when the yield of the reaction is superior to 90% and the sample to be dated is more than 5000 years old.

For the younger samples, isotopic fractionation of NBS oxalic acid should not be neglected, as shown in Table 2.

#### AKNOWLEDGMENT

The author is grateful to Minze Stuiver and Henry Polach for helpful teaching, and to Hans Oeschger for very helpful cooperation.

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

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	1,150	1,195	4
SPC - 47	2,550	2,550	1.6
SPC - 20	4,260	4,260	1.2
SPC - 6	7,950	7,990	0.5
SPC - 131	15,730	15,780	0.3
SPC - 43	28,050	28,080	0.1

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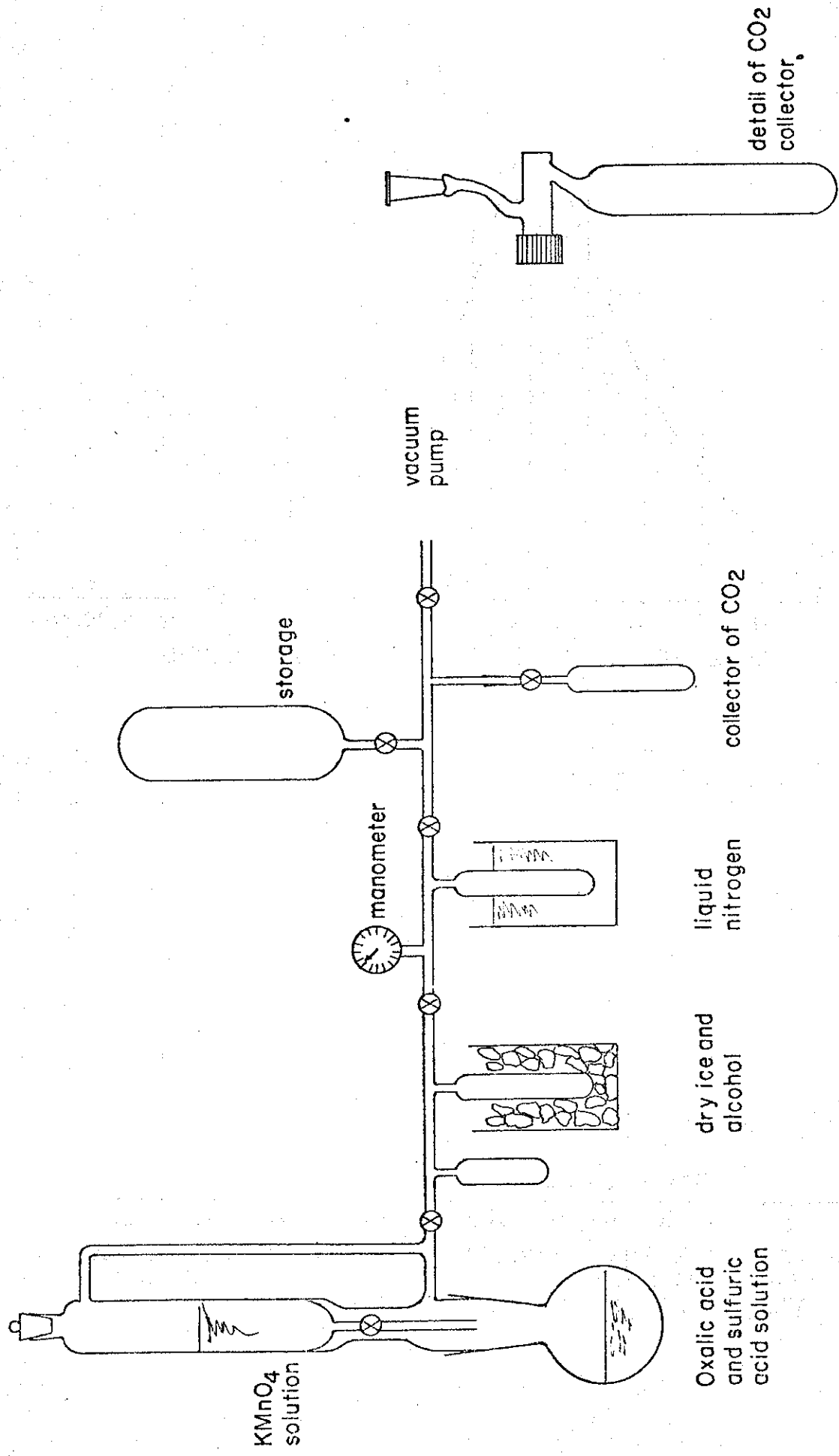


Fig. 1 - LINE OF OXIDATION OF OXALIC ACID WITH POTASSIUM PERMANGANATE AND RETIRING OF CARBON DIOXIDE

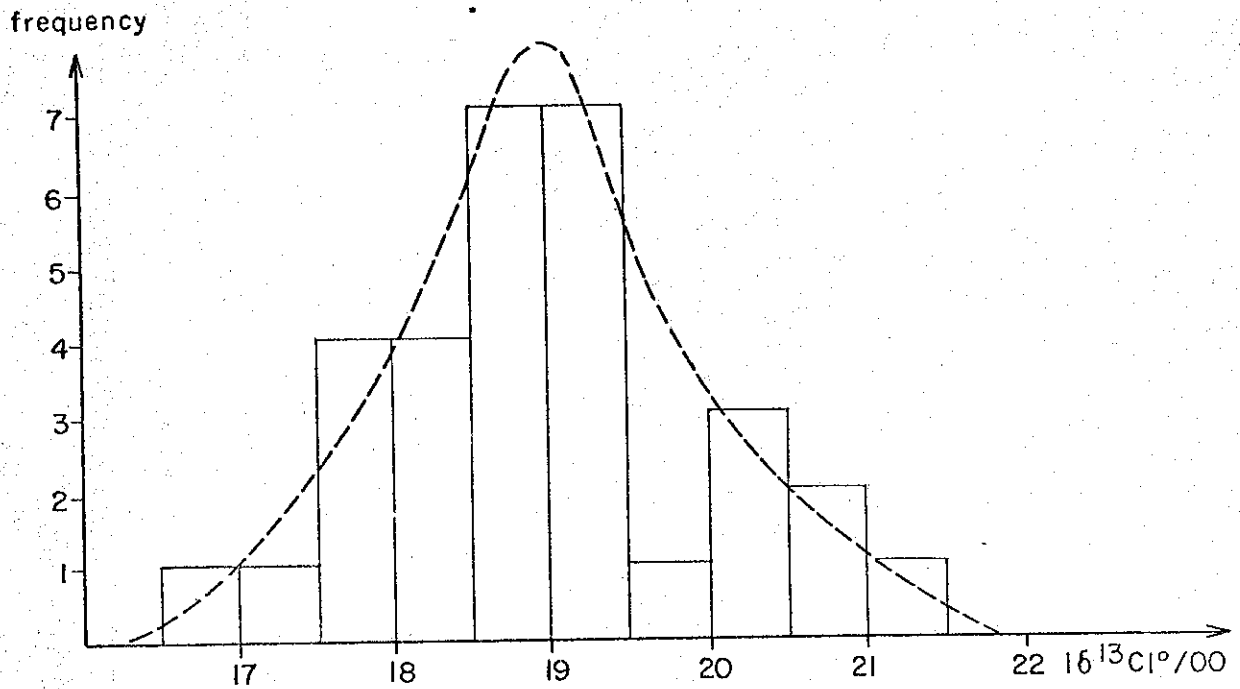


Fig. 2 - HISTOGRAM OF  $\delta^{13}\text{C}$  OF NBS OXALIC ACID

percentage error at the calculated age

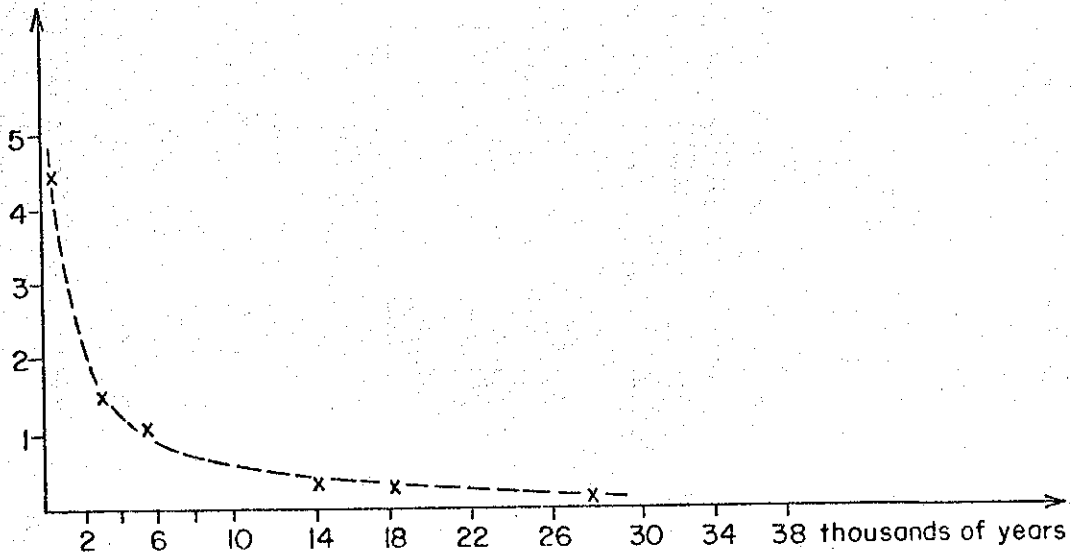


Fig. 3 - DIAGRAM OF PORCENTUAL ERRORS IN THE CALCULATED AGE OF MATERIALS CAUSED BY ISOTOPIC FRACTION OF OXALIC ACID IN FUNCTION OF THE AGES OF MATERIALS