WET OXIDATION OF OXALIC ACID USED IN RADIOCARBON DATING AND 14C FRACTIONATION DURING THE OXIDATION

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ABSTRACT

A wet oxidation method of oxalic acid standard used in radiocarbon dating is described, and error due to possible carbon isotope fractionation during the oxidation is estimated.

INTRODUCTION

A recent article by Grey et al[1] pointed out the possibility of carbon isotope fractionation during wet oxidation of oxalic acid standard. The difficulty of determining completion of the reaction between oxalic acid and potassium permanganate in acidic medium was also discussed. However, they did not outline the procedure for complete oxidation nor the procedure employed in their studies.

The chemical reaction for the generation of carbon dioxide is used in quantitative analytical chemistry for the standardization of potassium permanganate solution, and the stoichiometric reaction involved is:

$$5C_2O_4^{--}+2MnO_4^{-} \longrightarrow 10CO_2+Mn^{++}+8H_2O.$$
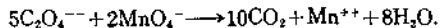
A procedure for the wet oxidation of oxalic acid has been described by Kolthoff and Sandell[2] in which the end point is easily detected, and the amount of potassium permanganate required to oxidize a given amount of oxalic acid can be calculated and an excess can be added to insure complete carbon dioxide generation.

EXPERIMENTAL METHODS

A. WET OXIDATION OF THE OXALIC ACID

The oxidation procedure used in this study is a scale-up adaptation of that described by Kolthoff and Sandell[2]. The amount of MnO_4^- required to oxidize a given amount of oxalic acid is calculated according to the stoichiometric reaction involved. These calculations show that 1.0 g of the NBS oxalic acid standard(our analyses showed that this acid is dihydrate and at least 99.9% pure) requires 0.50g of $KMnO_4$ for oxidation. A procedure for the complete liberation of CO_2 from the standard oxalic acid consists of dissolving 18 g of oxalic acid in 300ml of 5% H_2SO_4 (v/v) and slowly adding 10g(11% excess) of reagent grade $KMnO_4$ in aqueous solution. The complete generation of CO_2 is easily recognized by the color change from clear to dark brown. The evoled CO_2 is used for benzene synthesis according to Noakes, Kim, and Akers[3] and the specific activity measured.

B. 14C FRACTIONATION DURING THE WET OXIDATION

In order to study possible fractionation, a large amount of oxalic acid (54 g) was used, and CO_2 was genrated as described above. The CO_2 was separated into three sequential fractions of equal size by adding onethird of the stoichiometric amount of $KMnO_4$ for each of the first and second fractions: for the final

fraction, an excess of $KMnO_4$ was added to insure the complete generation. The first and the last fractions were used for benzene synthesis and the specific activity was measured.

RESULTS AND DISCUSSION

Table 1 shows the results of each fraction compared with the specific activity of a total sample of oxalic acid oxidized to completeness.

TABLE 1. Specific activity of synthesized benzene

Sample	95% of specific activity (c/m/g of C)
Complete oxidation 1	7.63±0.05
Complete oxidation 2	7.57±0.05
First fraction	7.37±0.05
Second fraction	Discarded
Third fraction	7.82±0.05

These results confirm those of Grey et al[1], which showed that ^{14}C fractionation can occur during the wet oxidation process; however, 16% error in ^{14}C measurement due to isotopic fractionation as pointed out by Grey et al[1] is highly improbable if one employs reasonable experimental conditions. This work shows that if only one-third of the CO_2 available is collected from the oxalic acid standard, the specific activity may be about 3‰ low. This value is comparable with the work of Lindsay, McElcheran, and Thode[4].

In this study, mass spectral analyses of stable carbon isotopes was not investigated since previous works[3,5] showed that carbon isotopic fractionation during the acetylene and benzene syntheses are negligible, and also it is a widely accepted fact that the stable carbon isotope ratio is used for monitoring of ^{14}C fractionation; therefore, ^{14}C specific activity measurement should be sufficient for the study of isotopic fractionation.

REFERENCES

1) D. C. Grey, P. E. Damon, C. V. Haynes, A. Long, *Radiocarbon*, v. 11, no. 1, (1969), 1.

2) I. M. Kolthoff, E. B. Sandell, *Textbook of Quantitative Inorganic Analysis*, The Macmillan Co., New York, (1952), p. 564.

3) J. E. Noakes, S. M. Kim, L. K. Akers, *Geochim. et Cosmochim Acta*, 31, (1967), 1094.

4) J. G. Lindsay, P. E. McElcheran, H. G. Thode, *J. Chem. Phys.*, 17, (1949), 589.

5) C. L. Hubbs, G. S. Bien, *Radiocarbon*, 9, (1967), 261.