

Radiocarbon

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CARBON-ISOTOPE FRACTIONATION DURING DRY COMBUSTION OF OXALIC ACID

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Grey *et al.* (1969) have discussed the problems that arise when using the wet oxidation method for the preparation of CO₂ from oxalic acid and suggest that, although offering an effective substitute, the dry combustion method also has problems.

Results obtained in this laboratory over the past 9 years indicate that only minor problems arise when using the dry combustion method.

Between January, 1961 and September, 1969, 47 oxalic acid standard CO₂ gas samples were prepared. Until January, 1968, C¹³/C¹² determinations were not available to the laboratory. However, anticipating that carbon isotope ratios would become available in the future, some CO₂ from randomly selected oxalic acid preparations was kept for future analysis. Thirteen such samples have been analyzed (by Isotopes Inc., New Jersey) dating from 1961 to January, 1969. The results are shown in Table 1.

TABLE 1
δC¹³ values for CO₂ from oxalic acid standards prepared by
the dry combustion method

Date of preparation	CO ₂ yield (%) (approx.)	C ¹³ (‰)* (Relative to PDB standard)
January, 1961	97	-19.4
July, 1962	96	-17.8
September, 1963	100	-18.4
January, 1964	100	-19.5
September, 1964	98	-18.3
January, 1965	100	-17.8
December, 1965	93	-18.2
August, 1966	96	-17.8
October, 1967—Analysis 1	97	-20.1
—Analysis 2	97	-20.2
1967-1968**	96	-18.2
November, 1968	93	-20.6
January, 1969	60	-26.9

* Analytical error for each determination is ± 0.2‰.

** The CO₂ gas on which this determination was carried out was made up of a mixture of 4 individual oxalic acids, prepared between August, 1967 and April, 1968.

It has been determined quantitatively, for the volume of the preparation line used in this laboratory, that the expected yield of CO₂ for an oxalic acid combustion is ca. 1.5 cms of CO₂ gas pressure/gm of dry oxalic acid in an expansion volume of 18.5 L. The approximate yields of CO₂ given in Table 1 were calculated on this basis.

The only result obtained that shows any appreciable amount of fractionation is the preparation of January, 1969 (60% yield). This reaction was stopped intentionally about halfway through completion in order to verify that incomplete combustion results in fractionation of carbon isotopes (Craig, 1961). With respect to the total of 47 CO₂ preparations from oxalic acid, only 4 had yields of less than 90%. Because of the "isotope-yield" correspondence, as is evident in Table 1, 2 of these preparations prepared after January 1969 were discarded and not used for counting purposes. It is now our policy to discard all preparations which do not give greater than 90% of the expected yield. Results show safety in assuming that only slight, or negligible, fractionation occurs if more than 90% of the oxalic acid is converted to CO₂. This should not deter workers from obtaining δC^{13} values as a routine policy, but should lend a little more confidence to the dry combustion method of producing CO₂ gas from oxalic acid.

Ignoring the final result (January, 1969) listed in Table 1, the average δC^{13} value is -18.9% , referred to the PDB standard, which agrees with the value of -19.0% determined by Craig (1961).

It was stated earlier that problems encountered in the preparation of CO₂ from oxalic acid by the dry combustion method used in this laboratory appear to be minor. Apart from the fact that the oxalic acid is given no pretreatment prior to combustion, only one change in the normal procedure for the preparation of other organic samples must be made. The normal procedure is fully described in Lowdon *et al.* (1969) and Lowdon and Blake (1970). For the successful preparation of CO₂ from oxalic acid, the temperature of the combustion furnace must be lowered from 700°C (for other organic samples) to 450°C, thus allowing the reaction to proceed very slowly. The reason for this change is not so much that a rapid reaction may enhance the chances of fractionation, but rather that a higher temperature causes rapid evaporation of the oxalic acid, giving rise to explosive mixtures in the combustion tube.

The results discussed here, and our experience have shown that the dry combustion method of preparing CO₂ from oxalic acid is reliable and gives reproducible results, provided time and care is taken to convert more than 90% of the carbon to CO₂. The major annoyance in the method is the length of time (ca. 4 hrs for 30 gms of oxalic acid) involved in sample preparation.

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