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A PROCEDURE FOR THE PREPARATION OF BENZENE FROM ^{14}C NBS OXALIC ACID STANDARD

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ABSTRACT. A simple procedure for the conversion of ^{14}C NBS oxalic acid standard to benzene without direct combustion or wet oxidation is reported. Fractionation in the synthesized benzene was not detected.

INTRODUCTION

The direct combustion or wet oxidation of ^{14}C NBS oxalic acid standard to carbon dioxide is the accepted technique used by most radiocarbon dating laboratories. Fractionation during these oxidations has been reported by many investigators. Grey and others (1969) reported $\delta^{13}\text{C}$ values of +61.5‰ for the last 0.6 percent fraction of carbon dioxide prepared from oxalic acid, and Polach and Krueger (1972) have established experimentally that $\delta^{13}\text{C}$ values range from -50‰ to +54‰ for significant proportions of the carbon dioxide resulting from permanganate oxidation of oxalic acid. This fractionation could be of serious consequence to laboratories without access to mass spectrometric $\delta^{13}\text{C}$ value determinations, because the error in ^{14}C activity of oxalic acid, based on an assumed -19‰ $\delta^{13}\text{C}$, may lead to systematic errors in age determinations.

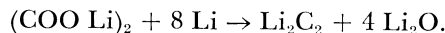
Recently, Valastro, Land, and Varela (1977) have reported an improved procedure for wet oxidation of the ^{14}C NBS oxalic standard. They also showed that negligible fractionation occurs when carbon dioxide and acetylene are converted to benzene, the counting liquid used by all radiocarbon dating laboratories with liquid scintillation facilities.

To overcome difficulties associated with these oxidation procedures, a technique in which lithium oxalate is converted to benzene, in very high yield, is reported.

PROCEDURE

For the preparation of approx 6 g benzene, 33.0 g ^{14}C NBS oxalic acid standard $(\text{COOH})_2 \cdot 2 \text{H}_2\text{O}$ is dissolved in 70 ml boiling distilled water. To this solution is carefully added a solution of lithium hydroxide prepared by reacting 3.62 g dry-packed lithium metal shot 4 to 16 mesh (weighed in a glove box flushed with dry nitrogen) with 125 ml carbon dioxide free water in an atmosphere of nitrogen. This latter solution can also be prepared by dissolving 12.5 g L.R. lithium hydroxide in 125 ml water.

The resulting solution is evaporated to dryness in a rotary evaporator and finally dried at 120°C. The yield of lithium oxalate is theoretical (26.7 g). This is mixed with 20 g dry-packed lithium metal in a stainless steel reaction vessel. Initially a vacuum is applied, but when the temperature reaches 100°C, the valve to the vacuum pump is closed, and the mixture reacted at 700°C and finally to 900°C using the method reported by Polach and Stipp (1967).



The lithium carbide is hydrolyzed with tritium free water, and the resulting acetylene, after purifying by passing over glass beads coated with saturated sodium hydroxide solution and 85 percent phosphoric acid, is polymerized at 5°C to benzene using vanadium-activated silica-alumina catalyst (Noakes, Kim, and Akers, 1967). When polymerization is complete, the benzene is removed from the catalyst by heating to about 150°C under vacuum and collecting the benzene in a small liquid nitrogen cooled trap. The recovered yield of benzene is greater than 95 percent. The purity of the benzene has been reported by Fraser and others (1974). The carbon dioxide obtained from three batches of benzene by burning the benzene in oxygen had an average $\delta^{13}\text{C}$ of $-19.6 \pm 0.4\%$.

CONCLUSION

The procedure outlined in this technical note gives benzene with the same isotopic concentration as ^{14}C NBS oxalic acid. This technique should prove particularly valuable for laboratories equipped with liquid scintillation spectrometers but without access to mass spectrometer $\delta^{13}\text{C}$ value determinations.

The procedure is easily carried out and eliminates many of the difficulties associated with direct combustion or wet oxidation techniques.

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