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THE ^{14}C CONTENT OF LITHIUM METAL USED IN BENZENE SYNTHESIS

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ABSTRACT. The lithium reagent used in the synthesis of benzene for ^{14}C dating contributes insignificant ^{14}C in high-precision measurements on 7 g benzene samples. Blank experiments on three different batches of lithium yielded small amounts of carbon, most of which probably originated as "memory" in the reaction vessel.

INTRODUCTION

Lithium metal reacts with CO_2 at 500°C to produce lithium carbide in the first step of benzene synthesis for liquid scintillation counting of ^{14}C (Polach, Gower and Fraser 1973). The reaction is:

$$10Li + 2CO_2 = Li_2C_2 + 4Li_2O \ .$$

Hydrolysis, the second step, starting at room temperature, yields acetylene:

$$Li_2C_2 + 2H_2O = 2LiOH + C_2H_2 \ .$$

Finally, the acetylene is catalytically trimerized to benzene. Any carbon impurity in the lithium may contaminate the benzene product, regardless of the initial oxidation state of the impurity. Carbonate, organic compounds or graphite might react with lithium to produce Li_2C_2. Polach, Gower and Fraser (1973) concluded that lithium shot stored out of contact with the atmosphere does not significantly contaminate samples for ^{14}C dating. Our laboratory is engaged in high-precision and high-sensitivity measurements of ^{14}C in natural materials, which could be adversely affected by small amounts of contaminant. Therefore we have reexamined the possibility of contamination from lithium.

At the Arizona Radiocarbon Laboratory, we obtain our lithium from the FMC Corporation, Gastonia, North Carolina, in the form of extruded rods packed under argon. Commercial processing of the lithium involves the following steps (S. K. McKenzie, personal communication 1991):

1. electrolysis, precipitating Li onto graphite electrodes
2. melting and casting in an argon atmosphere
3. cutting of ingots in air in a dry room
4. storage of ingots under mineral oil
5. extrusion and cutting of rods, with exposure to air in a dry room
6. packaging under argon.

In the laboratory, lithium is exposed briefly to air as it is weighed and transferred to reaction vessels. Possible sources of carbon impurity therefore include graphite electrodes, mineral oil and atmospheric CO_2.

Lithium exposed to the atmosphere may also react with N_2. The nitrogen content of a batch of lithium is therefore an indicator of degree of atmospheric exposure. FMC analyzes each batch of lithium for nitrogen, and will supply a certificate of analysis on request.

Between 1992 and 1995, we monitored the total C and ^{14}C produced from three different batches of lithium rod. For each batch we conducted a blank run using 35 ± 2 g lithium, which is the amount normally used for conversion of 7 to 8 g of carbon (in CO_2) to benzene.

METHODS

The stainless steel reaction vessel was cleaned by scrubbing with steel wool, washing with deionized water and drying. The lithium was placed in the vessel, which was closed, then evacuated while being heated to 400–500°C. The reaction vessel was allowed to cool to room temperature overnight. Deionized water was introduced into the vessel, and the small amount of acetylene formed as a result was purified in a vacuum line by standard techniques. The acetylene was transferred to a sealed tube made from 6 mm OD Vycor™ containing 1 g CuO wire. Both the Vycor™ and the CuO wire had previously been baked in air to remove CO_2. The tube was heated at 850°C for 2 h. The resulting CO_2 was separated from H_2O at −80°C, and $\delta^{13}C$ was measured when possible. The CO_2 was converted to graphite (Slota *et al.* 1987) and the ^{14}C content was measured by accelerator mass spectrometry. In one case, the CO_2 sample was extremely small, and was diluted 1:1 with "dead" CO_2 before conversion to graphite.

RESULTS AND INTERPRETATION

Values of carbon yield, $\delta^{13}C$, percent modern carbon and nitrogen content are listed in Table 1.

TABLE 1. Analytical Data

Date, Lab codes	Weight Li (g)	Yield C (μmol)	pMC	$\delta^{13}C$ (‰)	N (ppm)
1992 A-6988 AA-9975	35.2	71.4	67.5 ± 0.5	−24.6	53
1993 A-7121 AA-10514	37.4	1.2	50.5 ± 0.7	too small	n.a.*
1995 A-8391 AA-17650	33.3	163	88.7 ± 0.4	−19.6	133

*Not available

The experiment with the 1995 batch of Li yielded the largest amount of carbon and the highest value of pMC. Adding this carbon (1.96 mg at 88.7 pMC) to a hypothetical background sample (7 g carbon at 0.0 pMC) results in a mixture with 0.03 pMC. This can be compared with typical high-precision measurements from 8000 min of counting on 7 g benzene samples:

1. medieval wood, pMC = 90.0 ± 0.15
2. spectroscopic grade benzene, pMC = 0.14 ± 0.04 measured against mean background.

In neither case would the addition of the carbon from the 1995 lithium experiment introduce a significant error. Even in the second case, an addition of 0.03 pMC to the mean would be below detection.

The carbon yielded in the three experiments probably represents a mixture of carbon from the lithium with carbon contaminating the reaction vessel. Examination of the $\delta^{13}C$ and pMC data together may help with identifying sources. Mineral graphite and mineral oil are likely to have $\delta^{13}C < -20‰$ and pMC ≈ 0; atmospheric CO_2 would have $\delta^{13}C \approx -8‰$ and pMC > 100 if incorporated into the

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lithium without isotopic fractionation. "Memory" carbon from the reaction vessel would most likely have $\delta^{13}C < -15‰$, and a possible range of pMC values from 0 to > 100. This suggests that much of the carbon collected in the 1995 experiment, but perhaps less in the other experiments, was of "memory" origin. The 1992 experiment yielded carbon with lower pMC and $\delta^{13}C$ than in the 1995 experiment, consistent either with "memory" of an old sample, or with admixture of low-pMC carbon from the lithium. In both cases, carbon from the lithium is included in the total yield, and the experiments indicate negligible error arising from carbon supplied in the lithium.

A memory effect in a stainless steel reaction vessel has been observed in another context. To clean a vessel contaminated by a high-^{14}C sample, H. Haas (personal communication 1998) found it necessary to strip a layer of steel from the inner surface by electropolishing. Some of the sample carbon had sintered into the stainless steel. Such carbon is not strongly bound within the steel, and is easily exchanged during subsequent reactions.

Conclusion

Carbon contained in reagent lithium introduces insignificant error into high-precision measurements of ^{14}C on 7 g benzene samples. Lithium bearing up to at least 133 ppm N is acceptable as a reagent for benzene synthesis in high-precision ^{14}C dating by liquid scintillation counting.

References

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