

LA PLATA RADIOCARBON LABORATORY LIQUID SCINTILLATION COUNTING AND INTER-LABORATORY CHECK SAMPLES

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INTRODUCTION

The development and improvement of benzene synthesis for radiocarbon dating by liquid scintillation counting was started at LATYR in 1981. The basic technique employed was described by Polach, Gower & Frazer (1972). The line of benzene synthesis is similar to that used by Coleman *et al* (1972). The pretreatment of the samples and transformation to CO₂ has been previously described (Figini *et al*, 1984). The conditions of measurement were partially determined according to Pearson (1979). Results of measurements of interlaboratory check samples using the technique described are given.

MATERIAL AND METHODS

Benzene Synthesis

The conversion of 0.26 moles of CO₂ to Li₂C₂ is carried out in a stainless steel reactor in which are placed 20g of lithium metal shot, low sodium grade (produced by Lithium Corp of America), maintained in ether of petroleum anhydrous. This quantity is 100% in excess of the stoichiometric amount needed. After the reactor is closed and evacuated, the reaction is carried out by heating to 650°C in a furnace, maintaining a pressure of CO₂ to be absorbed into molten lithium at 56cm Hg for 20 min. In order to assure the total transformation at Li₂C₂, the reactor is heated to 1000°C for 30 min. Any extraneous gases are removed with a vacuum pump. When the reactor reaches room temperature, the lower part is cooled by dipping in a bath at 0°C. Under these conditions the hydrolysis of lithium carbide is performed by slowly adding (one hour) of 1.5L of distilled water. When normal yields of CO₂ to C₂H₂ are obtained (98 to 100%) the alkaline solution is clear. Occasionally, when yields were low, the solution turned black, with a few carbonaceous particles and encrustations at the bottom of the reactor. This clearly demonstrated that the predominant reaction had been the transformation in C and Li₂O. In some cases, the solution was whitish, indicating the formation of Li₂CO₃ by a secondary reaction (Belluomini *et al*, 1978) and with a strong NH₃ odor. This implies that air was introduced into the system through a leak in the vacuum (Griffin & Druffel, 1985).

The following vanadium catalyzers (Harshaw Chemical Co) were tested for the trimerization of C₂H₂ to C₆H₆, according to Coleman *et al* (1972): V-0301, T1/8; V-0501, T1/8; V-0601, T1/8. Also used as catalyzer support of cracking HFZ, Houdei 310m² according to Noakes, Kim & Akers (1967). In all these cases, benzene production was negligible. When we used

V-0701, T1/8 (Harshaw Chemical Co), the first trials rendered unequal yields. The best results were obtained by leaving the catalyzer (40g) in the oven at 550°C for more than 48 hr and transferring it while hot to the catalyst column, evacuating up to 10^{-3} torr. Following this procedure, the catalyzer was re-used effectively for more than 30 syntheses, with no evidence of memory effect. Trimerization was carried out at 0°C, maintaining a pressure of C_2H_2 of 76 ± 10 cm Hg on the catalyzer. Thirty minutes were sufficient for a reaction of 0.13 moles of C_2H_2 . The last trace of C_2H_2 was frozen into the column by submerging its end into liquid N_2 . The column was then isolated and left standing at room temperature overnight. The recovery of benzene was carried out by heating the catalyst column in a furnace, under vacuum, at 125°C for 2 hr. Chemical conversion yields for the CO_2 to C_6H_6 is $\approx 85\%$.

Measurement

Analysis of the final benzene samples for radiocarbon activity was performed in a Beckman LS-100 liquid scintillation spectrometer, using commercial Packard vials (20ml) of low potassium glass. Thirty vials were selected for their similarity of weight (Harkness & Wilson, 1972). In order to minimize evaporative loss through the standard vial seal, new seals were made with viton O-rings, a specially fitted PTFE stopper and a plastic screw cap. The glass vial was masked with black paint on white above the level reached by the top of the scintillation liquid so as to reduce cross-talk between counter photomultiplier tubes (Pearson, 1979).

A fraction (2ml) of the benzene sample was weighed (1.758g) out accurately into the counting vial. To this was added 0.5ml of a scintillation solution, composed of PPO and POPOP in scintillation grade toluene, with final concentrations in the vial of 5g/L and 0.05g/L, respectively. The medium value of the background (5.4cpm) and standard (13.5cpm) was individually determined for each of the vials. No memory effect was noticed during the alternate measurement of background and standard. The measurement was made at intervals of 100 min, alternating background, sample, and standard. The energy window for the measurement of ^{14}C was adjusted placing the lowest limit at the end of the 3H curve. The net counts were corrected for loss of weight and normalized to 1.758g. Benzene background was synthesized from acidification of $CaCO_3$ USP light (powder) TAC Mallinckrodt Art 4052. Benzene Merck Art 1783 was used for routine measurements. Standard benzene was synthesized from wet oxidation of the NBS oxalic acid (SRM 4990B), following the method of Valastro, Land and Varela (1977). For routine measurements, we used a standard prepared by dilution of benzene marked ^{14}C (supplied by Lab de Metrologie des Rayonnements Ionisants, Gif-Sur-Yvette, with an activity of 1.042×10^{-6} Ci/g), up to an activity equal to the standard of reference NBS oxalic acid. Date calculations were previously given (Figini *et al.*, 1984). No $^{13}C/^{12}C$ ratios were measured and results are not corrected for ^{13}C fractionation.

Sample descriptions are based on information provided by submitters.

INTER-LABORATORY CHECK SAMPLES

Norway

LP-72a. 9340 ± 210

Shells (*Mya truncata*) subm by Otto Salvigsen, Norsk Polarinst, dated at 9480 ± 140 (T-2919, OS, pers commun). *Comment:* another portion of the same sample was determined by gas counting at 9280 ± 250 (LP-72: R, 1984, v 26, no. 1, p 128).

New Zealand

LP-73a. Hollyford Valley 7890 ± 110

Shells (*Amphiderma* sp) from lower Holly Ford valley, SW corner, S Island, New Zealand. Subm by H S Jansen, Inst Nuclear Sci, DSIR, New Zealand, dated at 7670 ± 70 (R-9048, internal no. New Zealand lab, HSJ, pers commun). *Comment:* another portion of same sample was determined by gas counting at 7460 ± 210 (LP-73: R, 1984, v 26, no. 1, p 128).

France

LP-83. Le Grau du Roi 25644, Le Petit Travers, Hérault 7250 ± 100

Shells from oldest offshore bar, between Mangio pond and sea, at Le Grand Travers (43° 44' N, 4° 03' E). Subm by J Evin, CDAI, Lyon. Age reported was 7050 ± 100 (Ly-1511: R, 1979, v 21, no. 3, p 426).

Sweden

LP-101. Southern Baltic 4 9650 ± 90

Wood from large pine stump coll at 52m depth (55° 43' N, 14° 28' E). Subm by S Håkansson, Lund. Age given was 9420 ± 95 (Lu-890: R, 1976, v 18, no. 3, p 293).

LP-103. Kasi Mysuseter 4500 ± 100

Wood (*Pinus* sp) id by T Bartholin from bottom of unintentionally drained small lake near Kasi Mt, ca 1km N of Mysuseter (61° 49' N, 9° 40' E). Alt ca 1000m. Subm by S Håkansson. Age reported was 4890 ± 65 (Lu-995, SH, pers commun). *Comment:* both samples were pretreated in same manner as Lund lab (SH, pers commun).

United States

LP-134. Wisconsin 11,920 ± 140

Wood from Two Creeks interstadial, on W shore of Lake Michigan (44° 19' 40" N, 87° 32' W). Subm by A Long, Univ Arizona. Several dates between 11,700 to 12,200 BP (AL, pers commun).

CONCLUSIONS

The methodology we employed to obtain benzene is efficient and produces a radiochemically pure product. The operative form of the vanadium catalyzer (V-0701, T1/8) produces good results with higher yields of benzene when longer in the oven at 550°C. The catalyzer prepared by LATYR did not produce the desired results, probably due to the catalyzer support employed. The ^{14}C results of the inter-laboratory check samples agree with those determined by other laboratories.

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