

## USDA SEDIMENTATION LABORATORY RADIOCARBON DATES I

L. L. McDOWELL and M. E. RYAN

U. S. Department of Agriculture,\* Agricultural Research Service,  
Soil and Water Conservation Research Division, Oxford, Mississippi

The radiocarbon dating laboratory at the USDA Sedimentation Laboratory was established to supplement current watershed geomorphologic investigations. The principal objective of the program is to provide information on valley aggradation rates and sequences.

Liquid scintillation counting of benzene is employed (Tamers *et al.*, 1961; Noakes *et al.*, 1963; McDowell and Ryan, 1964). The chemical synthesis of benzene has been modified to increase the carbon yield and to decrease the man-hours required per sample.

All samples are visually inspected for contaminants, which are removed from the sample before chemical pretreatment. Wood and charcoal are washed with hot 3N NaOH, distilled water, hot 3N HCl, and finally with distilled water. Samples of peat, soil, and animal residues (size permitting) are subjected to more rigorous pretreatment resulting in the separation of crude fractions of "cellulose" and "lignin" (Olson and Broecker, 1958).

The general method for the synthesis of benzene from the original sample is given by the following reactions:

1. Sample + O<sub>2</sub> —————→ CO<sub>2</sub> + H<sub>2</sub>O
2. CO<sub>2</sub> + 2NH<sub>4</sub>OH —————→ (NH<sub>4</sub>)<sub>2</sub>CO<sub>3</sub> + H<sub>2</sub>O
3. (NH<sub>4</sub>)<sub>2</sub>CO<sub>3</sub> + SrCl<sub>2</sub> —————→ SrCO<sub>3</sub> + 2NH<sub>4</sub>Cl
4. 2SrCO<sub>3</sub> + 5Mg —————→ SrC<sub>2</sub> + SrO + 5MgO
5. SrC<sub>2</sub> + H<sub>2</sub>O —————→ C<sub>2</sub>H<sub>2</sub> + SrO
6. 3NaBH<sub>4</sub> + 4BF<sub>3</sub>(C<sub>2</sub>H<sub>5</sub>)<sub>2</sub>O —————→  
Diglyme  
2B<sub>2</sub>H<sub>6</sub> + 3NaBF<sub>4</sub> + 4(C<sub>2</sub>H<sub>5</sub>)<sub>2</sub>O
7. 3C<sub>2</sub>H<sub>2</sub>  $\xrightarrow[\text{silica-alumina}]{\text{B}_2\text{H}_6\text{-activated}}$  C<sub>6</sub>H<sub>6</sub>

Reactions 1 through 5 were employed by Suess (1954) in the synthesis of C<sub>2</sub><sup>14</sup>H<sub>2</sub> for radiocarbon dating. Reaction 4 is conducted in essentially the manner described by Suess, except for the ratio of SrCO<sub>3</sub> to Mg employed. Strontium carbonate, after heating to 600°C to remove traces of ammonia, is reduced to strontium carbide using a mixture of 92 g of SrCO<sub>3</sub> to 83 g of Mg powder (40 mesh). The carbon yield for Reactions 4 and 5 combined is now consistent at 95%. Five percent of this C<sub>2</sub>H<sub>2</sub> is lost, however, to cooled charcoal during the purification of the acetylene.

Reaction 6 is employed in the production of diborane (Brown and Tierney, 1958) for activation of the silica-alumina catalyst. Diborane is routinely produced in a hood-mounted manifold and passed continuously into

\* In cooperation with the University of Mississippi and Mississippi Agricultural Experiment Station.

columns containing the silica-alumina. The present system (McDowell and Ryan, *mss.*, in preparation) is designed to produce about 2 moles of diborane which is sufficient to activate 10 columns of silica-alumina. Each column (ca. 300 g silica-alumina) will yield about 4.5 g of  $C_6^{14}H_6$  (Reaction 7) for counting.

The counting is performed by a Packard "Tri-Carb" liquid-scintillation spectrometer (Model 314AS) equipped with two counting channels and operating at 840 volts with discriminator control settings of 110-500-1000 for AA', B, and C discriminators, respectively. The sample chamber is shielded by 4 in. of iron; additional shielding of the preamplifiers, multiplier phototubes, and counting chamber is provided by 2 in. of mercury (2100 lb).

The counting solution consists of benzene (3.2518 g) synthesized from the sample carbon and the scintillators PPO (0.5% by weight) and POPOP (0.02% by weight). The counting vial used for most of the measurements in this list is constructed of low-potassium glass cemented to an aluminum base with white epoxy glue. The vial (3.5-cc capacity) was designed to provide a better relationship between the background counting rate and counting efficiency. The background counting rate for this vial is 2.34 cpm at about 50% counting efficiency. Presently, old samples, sample size permitting, (16 g  $C_6^{14}H_6$ ), are counted in a vial having a capacity of 17 cc with a background counting rate of 7.10 cpm at about 52% efficiency. The counting solution and chamber are cooled to about 8°C to reduce thermal noise in the multiplier phototubes.

Quenching checks are made on each sample of benzene using the ratio of counting rates observed in the two channels of the spectrometer.

The contemporary carbon standard, taken as 95% of the activity of the NBS oxalic-acid standard, is 7.04 cpm/g carbon. This value is in agreement with values determined for pre-1900 wood corrected to A.D. 1950 (see date list). Data have been calculated on the basis of a  $C^{14}$  half-life of 5570 yr in agreement with the decision of the Fifth Radiocarbon Dating Conference (Godwin, 1962). Errors listed include the standard deviations ( $1 \sigma$ ) of the counting rates of the contemporary samples, the unknown samples, and the background. Calculated errors less than 100 yr have been increased to that figure as a minimum.

Corrections have not been made for isotopic fractionation in the synthesis of benzene. Previous mass-spectrometric  $C^{13}$  measurements on acetylene samples (Craig, 1953; Suess, 1954) showed a loss of  $C^{14}$  ranging from 1.5 to 3.5%. Since the overall carbon yield in the  $C_6H_6$  synthesis ranges from 50 to 60%, fractionation is possible. Repeated analyses of the same sample (see date list) indicate that fractionation is reproducible within the limits of the counting statistics; hence errors resulting from fractionation are minimal.

#### ACKNOWLEDGMENTS

We acknowledge the cooperation of the following radiocarbon dating laboratories who supplied interlaboratory check samples: USGS, Yale, Lamont, Shell, University of Michigan, and University of Texas. In addition, we are grateful for the technical assistance offered by Meyer Rubin, USGS, and J. J.

Stipp, Packard Instrument Company, Inc. We especially appreciate the loan of a print-out recorder and other electronic components by Packard Instrument Company, Inc.

### SAMPLE DESCRIPTIONS

#### I. CONTEMPORARY SAMPLES

##### Contemporary carbon series

Quadruplicate syntheses of  $C_6^{14}H_6$  were made from 3 different sources of contemporary carbon to determine the reproducibility of the chemical and counting procedures. All values have been corrected to A.D. 1950.

NBS Oxalic Acid  $C^{14}$  standard; 95% value

Sample No.	cpm/g Carbon
<b>OX-48.</b>	<b>7.10 ± 0.10</b>
<b>OX-72.</b>	<b>6.98 ± 0.10</b>
<b>OX-87.</b>	<b>6.99 ± 0.10</b>
<b>OX-89.</b>	<b>7.08 ± 0.10</b>
<b>Average</b>	<b>7.04 ± 0.05</b>

Wood from foundation post of Greenwade House, log cabin built in middle 1850's in Brazos River Valley near Whitney, Texas (31° 54' N Lat, 97° 23' W Long). Coll. 1950 by R. L. Stephenson; subm. by E. B. Jelks, Texas Archeol. Salvage Project, Univ. of Texas, Austin. *Comment*: sample subm. by J. J. Stipp as an interlaboratory standard. Dated by Univ. of Texas as Tx-43 (Univ. of Texas II).

Sample No.	cpm/g Carbon
<b>OX-62.</b>	<b>6.93 ± 0.10</b>
<b>OX-65.</b>	<b>7.06 ± 0.10</b>
<b>OX-67.</b>	<b>6.87 ± 0.10</b>
<b>OX-82.</b>	<b>6.90 ± 0.10</b>
<b>Average</b>	<b>6.94 ± 0.05</b>

Wood, *Quercus borealis*, from a tree cut in 1964 in Holly Springs Natl. Forest, Holly Springs, Mississippi (34° 27' N Lat, 89° 23' W Long). Tree showed 107 growth rings. Coll. 1964 and subm. by T. L. Price, U. S. Forest Service and L. L. McDowell, USDA, Oxford, Mississippi.

Sample No.	Tree Rings	cpm/g Carbon
<b>OX-78.</b>	<b>1857-1867</b>	<b>6.89 ± 0.10</b>
<b>OX-84.</b>	<b>1857-1867</b>	<b>6.89 ± 0.10</b>
<b>OX-69.</b>	<b>1877-1882</b>	<b>6.95 ± 0.10</b>
<b>OX-80.</b>	<b>1877-1882</b>	<b>6.89 ± 0.10</b>
<b>Average</b>		<b>6.90 ± 0.05</b>

*General Comment:* mean values for wood from the Greenwade House, Texas, and from the *Quercus borealis*, Mississippi are  $93.9 \pm 0.8\%$  and  $93.4 \pm 0.8\%$ , respectively, of the NBS oxalic-acid standard.

## II. INTERLABORATORY CHECK SAMPLES

**OX-1. White Pine Copper Mine, Michigan** **10,420  $\pm$  220**  
**8470 B.C.**

Spruce log from till exposed inside of kettle, White Pine Copper Mine, N dam of S Tailings Pond, 500 ft E of former bed of Caribou Creek, near center NE  $\frac{1}{4}$  NE  $\frac{1}{4}$ , Sec. 2, T 50 N, R 42 W ( $46^\circ 45'$  N Lat,  $89^\circ 34'$  W Long), Ontonagon County, Michigan. Coll. 1960 and subm. by F. J. Brandtner. *Comment* (L.L.M.): interlab. check, dated by USGS as W-964,  $10,230 \pm 280$  (USGS VII).

**OX-2. Brønlund Fjord, Greenland** **5050  $\pm$  130**  
**3100 B.C.**

Driftwood from alt 35 ft on surface of marine terrace, 2 mi NE of Kap Harold Moltke ( $82^\circ 10'$  N Lat,  $29^\circ 50'$  W Long), E end of Brønlund Fjord, N Greenland. Terrace is formed of silt with thin veneer of stones. Coll. 1957, 1960 and subm. by W. E. Davies. *Comment* (L.L.M.): interlab. check, dated by USGS as W-1073,  $4970 \pm 260$  (USGS VII).

**OX-3. Promontory Point, Utah** **20,400  $\pm$  420**  
**18,450 B.C.**

Wood from large gravel pit on S tip of Promontory Point ( $41^\circ 14'$  N Lat,  $112^\circ 29'$  W Long), Boxelder County, Utah, W of Ogden. Tremendous exposures were made in the sediments of Lake Bonneville in order to obtain material for this new embankment of the Southern Pacific R.R. across Great Salt Lake. Three gravel pits were created at near-Provo levels. Samples were collected from above the middle-elevation spit, but stratigraphy was so disturbed by the pit operation that the relation of the bog deposits, from which the wood came, to the spit is questionable. Wood is from bog deposits 600 ft S of W-875 and at ca. 4775 ft alt. Coll. 1959 by J. R. Rubin and M. Rubin. *Comment* (L.L.M.): interlab. check, dated by USGS as W-876,  $20,600 \pm 500$  (USGS V).

**OX-4. Mesters Vig, Greenland** **7280  $\pm$  140**  
**5330 B.C.**

Driftwood from NE slope, cut bank at N tip of second delta section NW of Tunnelev, at Hestekoeno, alt  $19$  to  $20 \pm 1$  m. Coll. 1960 and subm. by A. L. Washburn, Yale Univ. *Comment* (L.L.M.): interlab. check, dated by Yale as Y-879,  $7460 \pm 130$  (Yale VII).

**OX-43. Mesters Vig, Greenland** **900  $\pm$  120**  
**A.D. 1050**

Driftwood from NE slope, inner edge of emerged strandline on delta at Noret outlet of Tunnelev, at Korsbjerg, alt  $3 \pm 0.5$  m. Coll. 1960 and subm. by A. L. Washburn. *Comment* (L.L.M.): interlab. check, dated by Yale as Y-702,  $735 \pm 110$  (Yale VII).

## III. GEOLOGIC SAMPLE

**OX-55. Oxford, Mississippi****5010 ± 100  
3060 B.C.**

Wood from excavation made on Highway 6 Bypass during construction of a box bridge on Burney Branch, NE  $\frac{1}{4}$  SE  $\frac{1}{4}$  Sec. 28, T 8 S, R 3 W (34° 22' N Lat, 89° 31' W Long). From log imbedded in silt loam soil (ca. 2% organic matter) 10 ft below surface of creek and 18 ft below floodplain. The silt-loam soil is covered by 8 ft of recent alluvium (principally sand and silt low in organic matter) probably deposited since 1835 when area was first opened to settlement (Happ *et al.*, 1940, p. 4; Hilgard, 1860, p. 293). Coll. and subm. in 1964 by Russell Woodburn, Univ. of Mississippi. *Comment*: date may represent age of old pond or creek deposit. Age is the average of two determinations:

OX-55	4980 ± 100
OX-77	5040 ± 100

## REFERENCES

## Date lists:

- |                     |                                        |
|---------------------|----------------------------------------|
| USGS V              | Rubin and Alexander, 1960              |
| USGS VII            | Ives, Levin, Robinson, and Rubin, 1964 |
| University of Texas | Tamers, Pearson, and Davis, 1964       |
| Yale VII            | Stuiver and Deevey, 1962               |
- Brown, H. C., and Tierney, P. A., 1958, Reactions of Lewis acids of boron with sodium hydride and borohydride: *Jour. Am. Chem. Soc.*, v. 80, p. 1552-1558.
- Craig, Harmon, 1953, The geochemistry of the stable carbon isotopes: *Geochim. et Cosmochim. Acta*, v. 3, p. 53-92.
- Godwin, H., 1962, Half-life of radiocarbon: *Nature*, v. 195, p. 984.
- Happ, S. C., Rittenhouse, Gordon, and Dobson, G. C., 1940, Some principles of accelerated stream and valley sedimentation: U. S. Dept. of Agriculture, Tech. Bull. no. 695, p. 133.
- Hilgard, E. W., 1860, Report on the geology and agriculture of the State of Mississippi: Jackson, Mississippi, p. 391.
- Ives, P. C., Levin, Betsy, Robinson, R. D., and Rubin, Meyer, 1964, U. S. Geological Survey radiocarbon dates VII: *Radiocarbon*, v. 6, p. 37-76.
- McDowell, L. L., and Ryan, M. E., 1964, Radiocarbon dating by liquid scintillation spectrometry: the synthesis of benzene (C<sup>14</sup>H<sub>6</sub>): U. S. Dept. of Agriculture, ARS-41-88.
- Noakes, J. E., Isbell, A. F., Stipp, J. J., and Hood, D. W., 1963, Benzene synthesis by low temperature catalysis for radiocarbon dating: *Geochim. et Cosmochim. Acta*, v. 27, p. 797-804.
- Olson, E. A., and Broecker, W. S., 1958, Sample contamination and reliability of radiocarbon dates: *New York Acad. Sci. Trans.*, v. 20, p. 593-604.
- Rubin, Meyer, and Alexander, Corrinne, 1960, U. S. Geological Survey radiocarbon dates V: *Am. Jour. Sci. Radioc. Supp.*, v. 2, p. 129-185.
- Suess, H. E., 1954, Natural radiocarbon measurements by acetylene counting: *Science*, v. 120, p. 5-7.
- Stuiver, Minze, and Deevey, E. S., 1962, Yale natural radiocarbon measurements VII: *Radiocarbon*, v. 4, p. 250-262.
- Tamers, M. A., Stipp, J. J., and Collier, J., 1961, High sensitivity detection of naturally occurring radiocarbon: chemistry of the counting sample: *Geochim. et Cosmochim. Acta*, v. 24, p. 266-276.
- Tamers, M. A., Pearson, F. J., Jr., and Davis, Mott, 1964, University of Texas radiocarbon dates II: *Radiocarbon*, v. 6, p. 138-159.