

UNIVERSITY OF ROME CARBON-14 DATES XI

M. ALESSIO, F. BELLA, S. IMPROTA

Istituto di Fisica, Università di Roma

G. BELLUOMINI, C. CORTESI, and G. L. MANELLI

Istituto di Geochimica, Università di Roma

During the last few years, we have set up the benzene scintillation method in our laboratory. C^{14} activity measurements are now carried out with both liquid scintillation and CO_2 -proportional counters. Chemical apparatus for benzene synthesis and a liquid scintillation spectrometer for low-level counting were built and are described below.

After standard pretreatment, carbon is converted to CO_2 by combustion or acid treatment and then synthesized to liquid benzene in a closed system for ca. 8 hours. The combustion line was set up after Broecker *et al.* (1959), connected with a benzene synthesizing line designed as suggested by Noakes *et al.* (1963; 1965; 1967), as well as with new designs and operating features (Alessio *et al.*, 1970b).

Converting a sample to CO_2 requires 90 to 120 min., yielding from 95% to 98% CO_2 . For the conversion of CO_2 into C_6H_6 , Table 1 shows reactions, time, and yields.

TABLE I
Benzene synthesis

Reactions	Yields (%)	Time (min.)
a) $\left\{ \begin{array}{l} 2 CO_2 + 10 Li \longrightarrow Li_2C_2 + 4 Li_2O \\ 2 C + 2 Li \longrightarrow Li_2C_2 \end{array} \right\}$		60-90
b) $Li_2C_2 + 2 H_2O \longrightarrow C_2H_2 + 2 LiOH$ catalyst	98-100	20-30
c) $3 C_2H_2 \longrightarrow C_6H_6$	98-100	180-240

a) In synthesis of Li_2C_2 metallic lithium pellets are used, in 10% > stoichiometrically required quantity. The metal is slowly brought to melting (ca. 600°C), completed in 15-20 min.; subsequently the temperature rises to ca. 800°C and lithium assumes an orange-red color. It was found that, keeping the temperature at ca. 800°C for > 15-20 min. after the total disappearance of CO_2 , the C_6H_6 yield is further raised to ca. 95% (Polach and Stipp, 1967).

The reaction completed, all traces of radon are removed by keeping the reactor bottom under vacuum at ca. 600°C for 30 min. The lithium carbide synthesis reaction is quantitative and fairly fast: not > 90 min. is required to convert 10 L CO_2 .

b) Distilled water is made to flow at ca. 200 ml/min. over lithium carbide at room temperature, at the same time cooling the bottom of reaction chamber, reaction being exothermic. Acetylene is frozen in

liquid nitrogen; water vapor, ammonia compounds, and hydrogen are suitably removed.

c) For trimerization of acetylene to benzene, a catalyst developed by Noakes *et al.* (1967) was used initially, consisting of 20% V_2O_5 on a silica-alumina support with a minimum specific surface of 200 m^2/g . Immediately before use, the catalyst was activated at ca. 300°C under rotary pump vacuum for 2 hours, while cycling reaction was carried out at $13 \pm 1^\circ C$, for at this temperature reaction kinetics were faster (Alessio *et al.*, 1970b). This catalyst could be reactivated several times by heating to ca. 300°C under vacuum for 2 hours, with yields always $> 90\%$ and high reaction kinetics.

At present our laboratory uses the KC-Perlkatalysator Neu catalyst, Kaly-Chemie A. G., Hannover. This product is activated to ca. 350°C for 15-20 min., while the temperature of acetylene to benzene trimerization begins at ca. 50°C, allowing reaction to proceed spontaneously. It was found that 100g of this non-regenerative catalyst is sufficient to produce up to 5.5ml benzene and all gas-chromatographic analyses of samples have always shown a degree of purity from 99.5 to 100%.

In a pyrex counting vial 4.5ml liquid is introduced, containing 2ml sample benzene and 2.5ml NE 216 liquid scintillator produced by Nuclear Enterprises Ltd. The cylindrical vial, ca. 1/3 as high as its diam., is inserted coaxially into a light pipe, to the ends of which are connected 2 photomultipliers operating in coincidence.

An anti-coincidence shield is formed by a plastic scintillator enclosing a light pipe and connected with a 3rd photomultiplier operating in anti-coincidence with the first two. The scintillation spectrometer is in a room at 18°C and is protected against soft component of cosmic radiation by a 20cm iron and 15cm lead shield. Data are recorded by an electronic unit incorporating coincidence circuits with 7 ns resolution times. Each activity measurement lasts ca. 24 hours, with regularity checks at 30-min. intervals. Background is 6.47 ± 0.04 cpm, the net modern activity 13.43 ± 0.08 cpm, and the figure of merit $E^2/B = 580$.

This list includes age measurements of check samples and of new series of Italian geologic and historic samples made by the liquid scintillation method.

As in dating with CO_2 -proportional counters in preceding lists, "modern standard" is wood grown near Rome from 1949 to 1953, whose activity was repeatedly checked with 95% of the activity of NBS oxalic acid. Errors quoted are 1σ statistical error. Ages were calculated using the Libby half-life of 5568 yr, with 1950 as the standard year of reference.

ACKNOWLEDGMENTS

We wish to thank the Consiglio Nazionale delle Ricerche for providing partial financial support. We also thank our technicians for their devotion and skill in developing the chemical equipment: A. Pellizzoni, M. Dante, and L. Lucidi for mechanics and O. Fogù for glassblowing.

SAMPLE DESCRIPTIONS

I. CHECK SAMPLES

The liquid scintillation method was checked, using for benzene synthesis CO_2 obtained from various samples dated with the proportional counter. Ages obtained from both methods agree satisfactorily and are compared in Table 2.

TABLE 2
Check samples

Sample	C^{14} age liquid scintillation method	C^{14} age CO_2 -proportional counting method	References
R-716	$28,500 \pm 2000$	$27,800 \pm 800$	R., 1971, v. 13, p. 404
R-578	$12,650 \pm 250$	$11,820 \pm 120$	R., 1971, v. 13, p. 406
R-703	5000 ± 70	4360 ± 50	R., 1971, v. 13, p. 407
R-706	$11,500 \pm 200$	$11,800 \pm 100$	R., 1971, v. 13, p. 407
R-594	8480 ± 200	8400 ± 70	R., 1971, v. 13, p. 409
R-595	5850 ± 160	5880 ± 50	R., 1971, v. 13, p. 409
R-375	3230 ± 100	3360 ± 50	R., 1973, v. 15, p. 165
R-375 α	3840 ± 80	3160 ± 50	R., 1973, v. 15, p. 165
R-831A α	1730 ± 90	1710 ± 50	R., 1973, v. 15, p. 169
R-834 α	1650 ± 90	1700 ± 50	R., 1973, v. 15, p. 169
R-836 α	1760 ± 100	1680 ± 50	R., 1973, v. 15, p. 169
R-823	$16,400 \pm 400$	$16,390 \pm 180$	R., 1973, v. 15, p. 173
R-825	$15,900 \pm 300$	$15,090 \pm 140$	R., 1973, v. 15, p. 173
R-707	3600 ± 90	3650 ± 50	R., 1973, v. 15, p. 175

II. GEOLOGIC SAMPLES

Italy

R-241. Ghiacciaio del Rutor **5570 \pm 120**
3620 B.C.

R-241 α . Ghiacciaio del Rutor **5950 \pm 130**
4000 B.C.

Brown-blackish peat with leaf remains (*Cyperaceae*, *Bryophyta*), and detritus with no wood, in terminal moraine of W branch of Rutor Glacier near confluence with E branch, 250m S Rutor Lake, Upper Valley Dora di la Thuile R., Valle d'Aosta, Piedmont ($45^\circ 39' 53''$ N Lat, $6^\circ 57' 24''$ E Long) at +2515m; coordinate system U.T.M. 32 TLR 42905910. Coll. 1958 by L. Peretti, and subm. 1966 by G. Charrier, both of Ist. Giacim. Min., Politecnico Turin. Peat is believed to come from an ancient peat bog, later covered and reworked by glacier, at foot of a high rocky shelf, at +2776m. Peat therefore provides evidence of a Rutor glacier terminal margin a few hundred m behind present one and glaciated area diminished $> 2\text{km}^2$, corresponding to a major Holo-

cene anathermic phase (Peretti, 1964). Pollen analysis of peat shows: *Pinus*, several species, (57.45%), *Abies* (34.44%), *Tilia* (2.75%) (Charrier, 1964). *Comment*: R-241 was pretreated with 10% HCl; R-241 α was given additional leaching with 6% NH₄OH. R-241 α date, indicating the climax of postglacial climatic optimum (Atlantic), substantially agrees well with pollen analysis showing predominance of *Abies* assoc. with *Pinus* and with characteristic mixed forest components (*Tilia*). Radiometric data, therefore, rule out other controversial reference to anathermic climatic phases of Late Holocene (Sub-Atlantic).

Other peat bogs and lacustrine deposits dated in various areas of the Alps to establish a chronology of postglacial climatic events (see: R., 1964, v. 6, p. 85-87; 1968, v. 10, p. 359-360; v. 12, p. 610-611).

Lago di Tenno series

Well-preserved trunks *in situ* on bottom of Tenno Lake, 4.5km N Tenno, prov. Trento, Trentino (45° 56' N Lat, 10° 49' E Long) at +570m. Coll. 1970 by Gruppo Sommozzatori di Riva del Garda and subm. by B. Bagolini, Mus. Tridentino Sci. Nat., Trento.

Trunks belong to submerged forest covering ca. 1/5 lake bottom on W side. Over 70 trees have been mapped by Mus. and are being id. by F. Pedrotti, Ist. Bot., Univ. Camerino. Samples dated with and without acid pretreatment (A-labelled samples): no carbonate present.

R-793. Lago di Tenno A **790 ± 70**
A.D. 1160

R-793A. Lago di Tenno A **1190 ± 80**
A.D. 760

Well-preserved, small trunk *in situ*. *Comment*: 2 dates do not agree well.

R-794. Lago di Tenno B **570 ± 70**
A.D. 1380

R-794A. Lago di Tenno B **630 ± 70**
A.D. 1320

Well-preserved, very small trunk or branch *in situ*. *Comment*: 2 dates agree.

R-795. Lago di Tenno C28 **1000 ± 70**
A.D. 950

R-795A. Lago di Tenno C28 **940 ± 70**
A.D. 1010

Well-preserved wood, ca. 25cm diam. trunk *in situ*. *Comment*: 2 dates agree.

General Comment: C¹⁴ dates, in particular R-794 ages, seem to confirm traditional belief that Tenno Lake basin was formed by a landslide ca. A.D. 1400 (Battisti, 1898; Tomasi, 1963; Untergasser, 1935; Venzo, 1935).

Pontelagoscuro series

In 1970, a water prospecting test, 60cm diam. and ca. 40m deep, was drilled by dry cable-tool method along Natl. Hwy. No. 16 about mid-way between Pontelagoscuro and Ferrara, Emilia (44° 51' 58" N Lat, 11° 36' 00" E Long) at +8.50m. Drill core was preserved for study. Later, at same location, a 3.5m diam. and 40m deep well was driven to trap aquifers located at depths 11 to 36m; 2 levels were found, 30.10 and 34.90m deep, rich in vegetable remains and 1 level, 35.70m deep, with abundant, large wood fragments. Coll. 1970 by drilling staff and subm. 1970 by M. Bondesan, Ist. Geol., Univ. Ferrara.

32,500 ± 2000**R-862. Pontelagoscuro 1****30,550 B.C.**

Vegetable remains, mainly small wood fragments, fairly well-preserved, from coarse sand level, 30.10m deep. *Comment:* sample pretreated with 10% HCl only because, despite slight darkening, test with 0.2N NaOH did not disclose humic material.

35,000 ± 3000**R-863 α . Pontelagoscuro 2****33,050 B.C.**

Vegetable remains, mainly small darkened wood fragments, found in coarse clayey sand 34.90m deep. *Comment:* sample was pretreated with 10% HCl and given additional leaching with 0.2N NaOH.

27,500 ± 1000**R-864. Pontelagoscuro 3****25,550 B.C.**

Fragment of well-preserved wood, 35cm long and 3cm diam., found in coarse clayey sand rich in large wood fragments, 37.70m deep. *Comment:* sample pretreated with 10% HCl only, as alkaline treatment was not considered necessary.

General Comment: as supposed, C¹⁴ dates indicate Würm age. However, dates cannot yet be fully interpreted since lithologic and paleontologic study of core has barely started; sedimentary environment and origin of dated materials have not yet been determined. In the area only known stratigraphy is from deep natural-gas prospecting well (Selli, 1945-46).

III. HISTORIC SAMPLES

*Italy***2100 ± 90****R-913. S. Andrea, Orvieto****150 B.C.**

Humic acids from brown earthy layer in archeol. excavations of a sacred area underlying St. Andrea's Church, Orvieto, Umbria. Coll. 1970 by M. P. Rossignani, and subm. 1971 by M. Cagiano de Azevedo, both of Ist. Archeol., Univ. Cattolica, Milan. *Comment:* layer containing scarce small bone fragments and charcoal appears as a final fire level indicating last stage of use of a sacred area of Villanovan-Etruscan age with superimposed foundations of a Palaeochristian basilica (Cagiano de Azevedo, 1972). Bones and charcoal being insufficient, humic acids

of layer judged uncontaminated by more recent carbon were dated; results are merely suggestive although they agree with expected archaeol. age.

REFERENCES

- Alessio, M., Bella, F., and Cortesi, C., 1964, University of Rome carbon-14 dates II: Radiocarbon, v. 6, p. 77-90.
- Alessio, M., Bella, F., Cortesi, C., and Graziadei, B., 1968, University of Rome carbon-14 dates VI: Radiocarbon, v. 10, p. 350-364.
- Alessio, M., Bella, F., Improta, S., Belluomini, G., Calderoni, G., Cortesi, C., and Turi, B., 1973, University of Rome carbon-14 dates X: Radiocarbon, v. 15, p. 165-178.
- Alessio, M., Bella, F., Improta, S., Belluomini, G., Cortesi, C., and Turi, B., 1970a, University of Rome carbon-14 dates VIII: Radiocarbon, v. 12 p. 599-616.
- 1970b, Report on the equipment and the activities of Rome University's carbon-14 dating laboratory: Quaternaria, v. 13, p. 357-376.
- 1971, University of Rome carbon-14 dates IX: Radiocarbon, v. 13, p. 395-411.
- Battisti, C., 1898, *Il Trentino*: Trento, Zippel Editore.
- Broecker, W. S., Tucek, C. S., and Olson, E., 1959, Radio-carbon analysis of oceanic CO₂: Internatl. Jour. appl. Rad. Isotopes, v. 7, p. 1-18.
- Cagiano de Azevedo, M., 1973, Un trionfo e una sconfitta: M. Volconio e Vulsinium: La Parola del Passato, in press.
- Charrier, G., 1964, Analisi pollinica della torba recentemente raccolta alla fronte del ghiacciaio del Rutor: Com. Glaccol. Italiano Boll., ser. 2, v. 14, p. 9-19.
- 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.
- Noakes, J. E., Kim, S. M., and Akers, L. K., 1967, Recent improvements in benzene chemistry for radiocarbon dating: Geochim. et Cosmochim. Acta, v. 31, p. 1094-1096.
- Noakes, J. E., Kim, S. M., and Stipp, J. J., 1965, Chemical and counting advances in liquid scintillation age dating: 6th internatl. conf. radiocarbon and tritium dating Proc., Pullman, Washington, June 7-11, 1965, p. 68-92.
- Peretti, L., 1964, Sulla presenza di torba nella morena deposta durante gli ultimi anni alla fronte attuale del ghiacciaio occidentale del Rutor: Com. Glaccol. Italiano Boll., ser. 2, v. 14, p. 1-59.
- Polach, H. A. and Stipp, J. J., 1967, Improved synthesis techniques for methane and benzene radiocarbon dating: Internatl. Jour. appl. Rad. Isotopes, v. 18, p. 359-364.
- Selli, R., 1945-46, La stratigrafia di un pozzo profondo perforato presso Pontelagoscuro (Ferrara): Gior. di Geol., ser. 2, v. 18, p. 53-72.
- Tomasi, D., 1963, *I laghi del Trentino*: Rovereto, Manfrini Editore.
- Untergasser, S., 1935, Elementi morfometrici del Lago di Tenno: Studi Trentini Sci. Nat., v. 16, p. 144-145.
- Venzo, S., 1935, Ricerche limnologiche trentine: il Lago di Tenno—Cenni geografico-geologici: Studi Trentini Sci. Nat., v. 16, p. 133-144.