

THE MEASUREMENT OF RADIOCARBON ACTIVITY AND SOME DETERMINATIONS OF AGES OF ARCHAEOLOGICAL SAMPLES

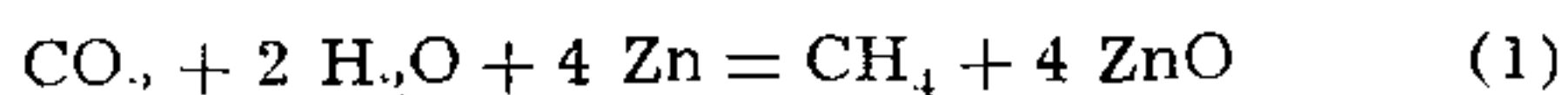
D. P. AGRAWAL, SHEELA KUSUMGAR AND D. LAL
Tata Institute of Fundamental Research, Colaba, Bombay-5

IN this paper, we present several radiocarbon dates of India based on archaeological samples, measured recently using a modified technique. So far, we had adopted the acetylene-gas proportional counting method developed by Suess (Suess, 1954). The preparation of acetylene, or of some suitable gas which offers good counting-characteristics, from the carbon atoms of the samples, is a necessary requirement for a sensitive counting of the activity of radiocarbon. The maximum energy of its beta-radiation is only 156 KeV and the solid source method of counting entails considerable errors and lack of precision. We have now developed a simple, rapid and quantitative method of synthesising methane gas from carbon atoms of the sample to be dated. The technique used is described briefly in this paper. Results of determination of fifteen "dates" of archaeological samples are also presented.

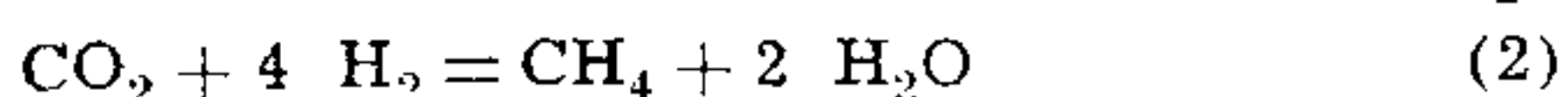
Previous determinations of radiocarbon "dates" of samples of archaeological and geological interest have been reported by us in three communications to this Journal (Agrawal *et al.*, 1964 a, 1964 b; Agrawal and Kusumgar, 1965). The "dates" are also presented annually in the Journal *Radiocarbon* which carries the results of world C^{14} -laboratories (Kusumgar *et al.*, 1963 a; Agrawal *et al.*, 1964 c).

SYNTHESIS OF METHANE

The technique is an adaptation of the methane synthesis method developed by Anand and Lal (1964) for purposes of counting tritium activity. Methane is synthesised from carbon dioxide gas produced from the sample carbon in a reaction vessel according to the following effective reaction:



Water and zinc react at 410°–420° C. to produce hydrogen which, in the presence of a catalyst (0.5% Ru on Al_2O_3), forms methane at > 475° C., by the following reaction with CO_2 :



The reaction (2) has been used for purposes of counting radiocarbon activity (Fairhall *et al.*, 1961), using commercially available hydrogen. For our synthesis, we have preferred to use

the reaction (1) since the hydrogen available to us was found to have enough tritium to give a net increase of more than one count per minute in the background rate. Tritium-free water, which provides the hydrogen atoms in the synthesised methane, was easily available to us from the tube-well at Chanasma (Gujarat). Its tritium activity was determined to be less than 1 T.U. which is expected to give an increase of not more than 0.02 c.p.m. in the background counting rate.

In order to make the reaction (1) quantitative, we use about 10% excess of water. The synthesis is carried out in a stainless steel reaction vessel (Fig. 1) of diameter 10 cm., and length 100 cm. Zinc dust (B.D.H.) and Baker's ruthenium catalyst* (Model E) are placed in dishes mounted on a self-supporting rod. Required amount of water is taken in a glass ampoule which is sealed and then mounted alongside the rod as shown in Fig. 1. The two furnaces are energised so as to raise temperatures of zinc and catalyst to 410°–420° and 490°–500° C. respectively. Typical proportions of the reactants are: 6.3 litres CO_2 (S.T.P.), 11 c.c. H_2O and 400 gm. zinc dust. Fifty grams of catalyst is taken which could be used satisfactorily for 12–14 syntheses. The reaction products are usually taken out after 15–20 hr. of energising the furnaces.

The purification of methane is carried out in a glass vacuum system shown in Fig. 1. Excess unconverted water is trapped in T_0 , kept at carbon dioxide-acetone slush temperature. The gases were then absorbed in liquid-air-cooled traps T_1 , T_2 and T_3 . Any traces of unconsumed CO_2 are trapped entirely in T_1 and T_2 . Methane, which is initially trapped in T_1 and T_2 , finally distils over to T_3 , since it has a vapour pressure of about 1.5 cm. Hg at liquid-air temperature. The vapour pressure of methane in T_3 which contains about 50 gm. high grade silica gel† (mesh size 12–28) is only a few microns. Pumping on T_3 for an hour with a liquid-air-cooled activated charcoal trap, T_4 , removes all

* Baker Plantium Division, Engelhard Industries Ltd., 52, High Holborn, London, W.C. 1.

† Davison Chemical, Baltimore, 3 Maryland.

traces of hydrogen present in the mixture. Synthesised methane is then distilled from trap T_3 to the liquid-air-cooled trap T_5 and expanded into a 10-litre flask. The completeness of the reaction is gauged by expanding the CO_2 found in traps T_1 and T_2 in a 5-litre flask. The amount of CO_2 left unconverted is usually found to be less than 5 c.c. (S.T.P.), corresponding to an yield of better than 99.9%.

COUNTING OF THE RADIOCARBON ACTIVITY

Two low-background Oeschger-Houtermans gas proportional counters (Houtermans *et al.*, 1957), of 2.7 litres volume, are used. The counters are filled with methane to pressures of 115 and 90 cm. Hg respectively to meet the requirements of archaeological dating. Relevant counting characteristics are given in Table I.

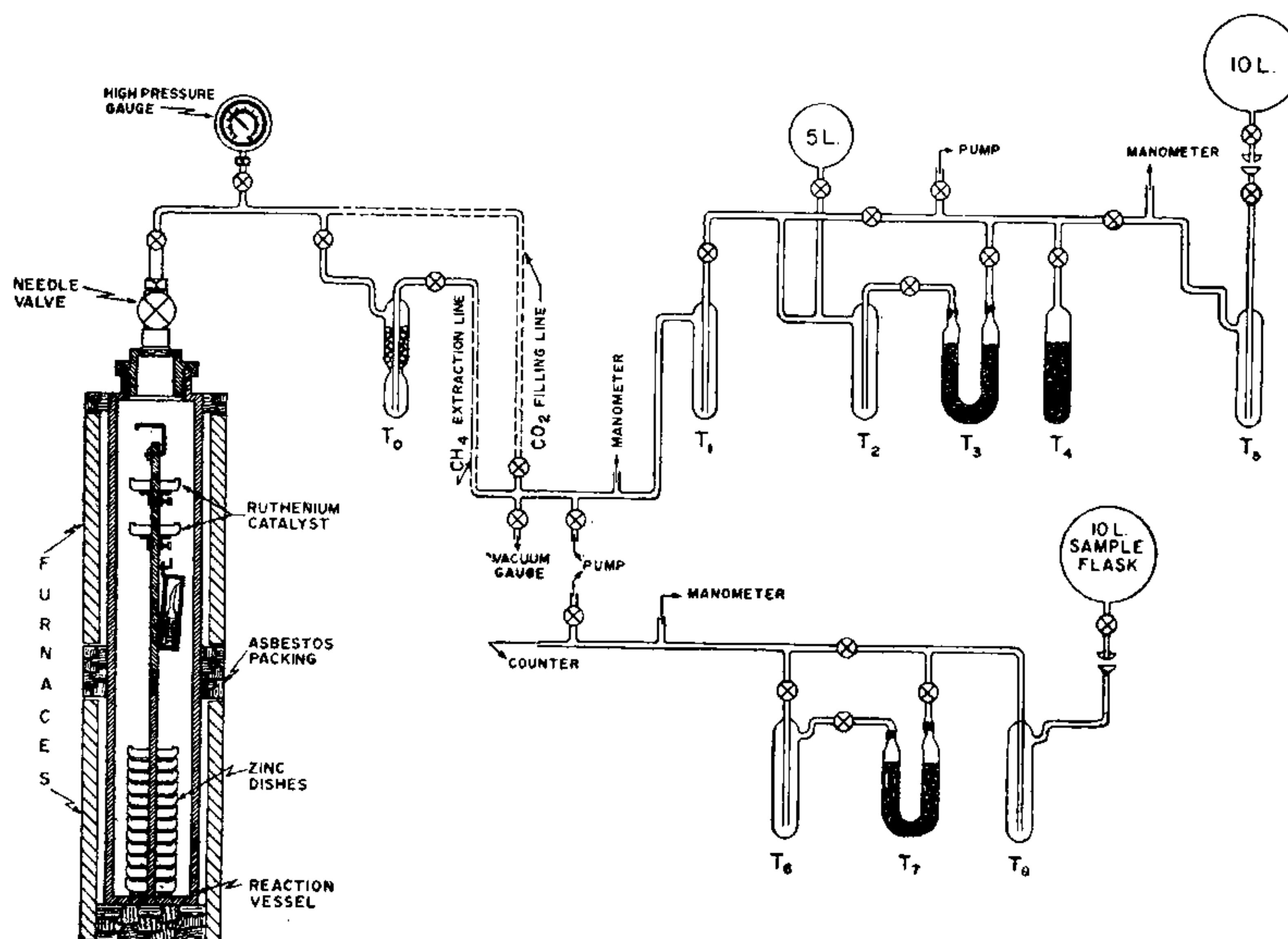


FIG. 1. A schematic diagram of methane synthesis and purification systems.

Before filling methane in the counter, a second purification of the sample gas is carried out. Methane is first trapped in liquid-air-cooled charcoal-silica gel (1:3 by volume) trap, T_7 , and then allowed to distil over to liquid-air-cooled trap, T_6 , by warming up T_7 to room temperature. A further purification is carried out by pumping on trap T_6 for fifteen seconds (Fig. 1).

We have not discussed here the method used for the preparation of CO_2 . The details of pretreatment of the sample and the generation of CO_2 from it have been described by Kusumgar *et al.* (1963 b). We still follow those procedures. However, additional purification steps for purification of CO_2 from any traces of H_2S , NO_2 , N_2O_5 , etc., have been introduced. CO_2 is passed successively through an aqueous solution of 0.1 M KMnO_4 containing 2% H_2SO_4 , silver wool at 300°C . and a charcoal-silica gel trap kept at room temperature.

TABLE I

	Counter I	Counter II
Filling pressure (cm. Hg)	115	90
Operating voltage	4.7 KV	4.4 KV
Background counting rate (c.p.m.) (Methane synthesised from "dead" carbon)	1.5	1.5
C^{14} -standard counting rate (total c.p.m.) (Methane synthesised from N.B.S. oxalic acid)	15.2	12.8

The effective amount of carbon counted in counters I and II is 0.91 gm. and 0.75 gm. respectively. Though the gas-filling pressure is higher by about a factor of two compared to that used previously by us for acetylene (Kusumgar *et al.*, 1963 b) the sensitivity is nearly the same since each molecule of methane contains only one carbon atom in contrast to acetylene which has two atoms per molecule. Higher gas pressures with methane, however, still provide low-operating voltages and it is

conveniently possible to increase the precision of the measurement by working at higher filling pressures. However, normally archaeological samples are available in small quantities only and therefore low-filling pressures were employed.

Main advantages in using the present method of methane counting over acetylene are: (a) rapid synthesis; (b) preparation of radon-free gas; and (c) the non-explosive nature of methane. With the acetylene method, steps for the preparation of strontium carbonate, strontium carbide, and acetylene usually took several days. It also was necessary to let the samples decay for a period of three weeks to make them free of radon activity. In the present system, the entire synthesis takes a day and no "wait" for decay of radon was found to be necessary.

The methane synthesis technique described above was adopted routinely since September 1964. Since then, six C^{14} -standard and seven background samples were prepared and counted. The counting rates were found to be the same within the statistical errors of measurements showing reproducibility both in counting as well as synthesis.

RESULTS

The measured "dates" of archaeological samples collected from the neolithic sites of the south, and a few N.B.P. Ware sites of the north are presented.† The dates are based on a value of 95% activity of the N.B.S. C^{14} -standard, for the modern C^{14}/C^{12} ratio. Two dates are given for each sample. The first one is calculated on the basis of 5568 ± 30 yrs. for the half-life of radiocarbon; the second date, given within brackets, is based on 5730 ± 40 yrs. for the C^{14} half-life. All dates are in years B.P.; to convert them to A.D./B.C. scale, 1950 A.D. should be used as the reference year.

For archaeological evaluation, all "dates" based on one of the values for C^{14} half-life should be used.

ACKNOWLEDGEMENTS

We are grateful to Shri H. L. N. Murthy and his colleagues for assembling the glass vacuum system and the high pressure line. Our thanks are due to Shri G. Rajagopalan for programming

the "age and error" calculations on the C.D.C. 3600 computer. We also acknowledge the assistance rendered by Shri P. S. Daudkhane during various phases of laboratory work.

C^{14} DATES WITH SAMPLE DESCRIPTIONS

Besnagar, Madhya Pradesh, India

TF-254, N.B.P. Ware Deposits, 2180 ± 105
(2245 ± 110)

Charcoal from Besnagar (Lat. $23^\circ 32'$ N., Long. $77^\circ 48'$ E.), District Vidisha, Trench BSN-I, Layer 8, Depth 2.70 m., Field No. BSN-I/GI/C/64-2. Sample submitted by A. Ghosh. Comment: The sample belongs to early phases of N.B.P. Ware at the site.

Bhaja, Maharashtra, India

TF-170, Buddhist Rock-Excavations, 350 ± 115
(360 ± 115)

Wood from "the girders supporting an arched roof", Bhaja (Lat. $18^\circ 44'$ N., Long. $73^\circ 29'$ E.), District Poona. NaOH treatment was also given. Submitted by Dr. K. A. Chowdhury. Comment: The sample was dated to help botanical studies on the decay of cell-walls. The divergent date is attributed by the submitter to the probability of the sample being derived from later repairs.

Karla, Maharashtra, India

TF-171, Buddhist Rock-Excavations, 2075 ± 100
(2135 ± 100)

Wood "from an inside rib fitted to the wall of a rock cave", Karla (Lat. $18^\circ 45'$ N., Long. $73^\circ 29'$ E.), District Poona. NaOH pretreatment was also given. Submitted by Dr. K. A. Chowdhury. Comment: The sample was dated to help botanical studies on cell-wall decay. Compare with BM-92, 2305 ± 155 (Barkar and Mackey, 1961) for the same structures.

Kausambi, Uttar Pradesh, India

Kausambi (Lat. $81^\circ 23'$ N., Long. $25^\circ 20'$ E.), now known as Kosam, District Allahabad, is situated on the bank of Yamuna. It is known as the capital of the later Pandavas. The site is being excavated by the Allahabad University under the direction of Prof. G. R. Sharma who submitted the samples.

TF-226, Rampart II, 2110 ± 95
(2170 ± 100)

Charcoal sample from Trench KSB-GR, Locus YZ3, 1-2, Layer 12, Depth 1.8 m., Field No. KSB/63/GR-138. Comment: The excavator's archaeological date bracket for the sample is ca. 535-185 B.C.

† The Radiocarbon Laboratory of the Tata Institute functions as a National facility for the determination of "ages" of important archaeological samples; communications for obtaining radiocarbon "dates" may be addressed to the Secretary, Radiocarbon Dating Committee, Tata Institute of Fundamental Research, Colaba, Bombay-5.

TF-219, Period III, 2325 ± 100
(2390 ± 100)

Charcoal from Trench KSBI-III-RD, Locus 2-7, Road I, Depth 3 m., Field No. KSB/63/AP-9. Comment: the sample has been attributed to the middle levels of N.B.P. Ware at the site.

TF-225, Period III, 2285 ± 105
(2350 ± 110)

Charcoal from Trench KSB-GR, Locus YZ3, 1-2, Layer 11, Depth 1.6 m., Field No. KSB/63/GR-136. Comment: The sample has been assigned to the early levels of N.B.P. Ware at the site.

TF-221, Period III, 2385 ± 100
(2450 ± 105)

Charcoal from Trench KSB-I-III-RD, Locus 5-7, Pit B sealed by Layer 12, Depth 4.3 m., Field No. KSB/63/AP-15. Comment: The excavator's date on archaeological considerations is ca. 400 B.C.

Mahanadi Bridge, Orissa, India

TF-252, Mahanadi River-Bed, 5815 ± 140
(5985 ± 145)

Drift wood from well No. 8, Depth 39 m., excavated during railway bridge construction work. NaOH pretreatment was also given. Submitted by K. Ramesh Rao, F.R.I., Dehra Dun.

Pataliputra, Bihar, India

TF-169, Wooden Palisades, 2005 ± 95
(2005 ± 100)

Wood from the Palisades of Kumrahar, from a depth of 5.4 m. NaOH pretreatment was also given. Submitted by Dr. K. A. Chowdhury. Comment: The sample archaeologically datable to Mauryan Period and was measured to help botanical studies on the decay of cell-walls.

Rajghat, Uttar Pradesh, India

TF-294, Black and Red Ware Deposits, 2190 ± 85
(2255 ± 90)

Charcoal from Rajghat (Lat. $25^{\circ} 18' N.$, Long. $83^{\circ} 1' E.$), District Varanasi, Mound I, Trench RGT-XIA, Locus X-XI, Layer 14, Depth 11 m., Field No. RGT-XIA 1963-64/S. No. 4. Submitted by A. K. Narain. Comment: Sample derives from disturbed strata.

Rupar, Panjab, India

TF-209, Period III, 2365 ± 100
(2435 ± 100)

Charred wood from Rupar (Lat. $30^{\circ} 58' N.$, Long. $76^{\circ} 32' E.$), District Ambala, Trench RPR-2, Locus X'-XI', Layer 30, Depth 11.4 m., Field No. RPR-2-3094. Submitted by A. Ghosh. Comment: Sample belongs to the early levels of Period III (ca. 500-400 B.C.) according to the excavator, Dr. Y. D. Sharma.

Tekkalakota, Mysore, India

Tekkalakota (Lat. $15^{\circ} 32' N.$, Long. $76^{\circ} 53' E.$), District Bellary, is an extensive neolithic site. The site was excavated by Deccan College and Post-Graduate Research Institute under the direction of H. D. Sankalia who submitted the samples. Comment: The radiocarbon dates show that Tekkalakota represents a later phase of neolithic economy. Unlike Utnur, whose antiquity goes to the close of III millennium B.C. (B.M. 54, 4250 ± 155) (Barkar and Mackey, 1960); TF-168, 3990 ± 115 ; TF-167, 4000 ± 115), available Tekkalakota C^{14} dates suggest a bracket of ca. 1800-1600 B.C. The three measurements from TKT-1 cluster around ca. 1600 B.C.

TF-277, Ash-Pit, 2220 ± 105
(2285 ± 110)

Charred grains from Trench A, TKT-GWD, Layer 2 ash-pit, Depth 0.3 m. NaOH treatment was also given. Comment (H. S. D.): Archaeological date uncertain as the sample is coming from an ash-pit.

TF-239, Neolithic Culture, 3395 ± 105
(3490 ± 105)

Charcoal from TKT-I, Trench I, Pit 4 sealed by 4, Depth 1.3 m. NaOH treatment was also given.

TF-237, Neolithic Culture, 3465 ± 105
(3565 ± 105)

Charcoal from TKT-I, Trench I, Layer 4, Depth 1 m. NaOH pretreatment was also given.

TF-262, Neolithic Culture, 3460 ± 135
(3560 ± 140)

Charcoal from TKT-I, Trench 9, Layer 1, Depth 0.25 m. (A few rootlets were present in the sample.) NaOH pretreatment was also given.

TF-266, Neolithic Culture, 3625 ± 100
(3730 ± 105)

Charcoal from TKT-II, Trench 2, Layer 2, Depth 0.17 m., Field No. 265. NaOH treatment was also given.

1. Agrawal, D. P., Kusumgar, S. and Sarna, R. P., *Curr. Sci.*, 1964 a, **33** (2), 40.
2. —, *Ibid.*, 1964 b, **33** (9), 266.
3. —, —, Lal, D. and Sarna, R. P., *Radiocarbon*, 1964 c, **6**, 226.
4. —, and —, *Curr. Sci.*, 1965, **34** (2), 42.
5. Anand, J. S. and Lal, D., *Nature*, 1964, **201** (4921), 775.
6. Barkre, H. and Mackey, C. J., *Radiocarbon*, 1960, **2**, 26.
7. —, *Ibid.*, 1961, **3**, 39.
8. Fairhall, A. W., Schell, W. R. and Takashima, Y., *Rev. Sci. Instr.*, 1961, **32**, 323.
9. Houtermans, F. G. and Oeschger, H., *Helvetica Phys. Acta.*, 1957, **31**, 117.
10. Kusumgar, S., Lal, D. and Sarna, R. P., *Radiocarbon*, 1963 a, **5**, 273.
11. —, — and Sharma, V. K., *Proc. Ind. Acad. Sci.*, 1963 b, **58**, 125.