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RUDJER BOŠKOVIĆ INSTITUTE RADIOCARBON MEASUREMENTS I

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The routine processing and measurement of samples in our Radiocarbon Laboratory began early in 1970 following a one-year testing period during which standard samples (anthracite and NBS oxalic acid) as well as samples of known age were prepared and measured. Our system is based on the studies of de Vries and Barendsen (1953), Fairhall *et al.* (1961) and Olson and Nickoloff (1965). However, several modifications of the cited methods were introduced and are briefly discussed below. A detailed description of the whole system will be published elsewhere (Srdoč *et al.*, 1970).

Samples are prepared before combustion by the standard method used in most radiocarbon dating laboratories. The samples are boiled in a 4% solution of HCl washed with distilled water, then left overnight in a 4% solution of NaOH heated at 80°C, washed and boiled in distilled water to neutrality and dried at 95°C. The sample thus prepared is burnt following the method described by de Vries (1953). The carbon dioxide is purified by passing over silver wool heated at 450°C. Nitrogen oxide is removed in an absorption tube filled with manganese dioxide. Carbon dioxide is collected in traps and transferred into the apparatus for conversion to methane. We applied the methane synthesis method of Fairhall *et al.* (1961), modifying the reactor vessel design to avoid any dead space.

The samples are stored after combustion and conversion to methane for 14 days and then counted twice for approximately 1000 min at roughly 10-day intervals.

The proportional counter consists of a steel tube 6 cm in diameter and 40 cm long. End insulators are machined from Araldite/CT 200, CIBA, Basel, Switzerland. The anode is a stainless steel wire 25.4 m_μ in diameter. A beryllium window having a high transmission for 6 keV X-rays allows counter calibration. Checking the counter gas for purity and setting the gas multiplication is performed by a routine procedure in our laboratory. This routine check consists in measuring the counter resolution and the position of the Fe^{55} peak (5.88 keV) with a multichannel analyzer. The guard counter consists of two concentric tubes divided into 18 separate counters by means of radially inserted metal sheets. The guard counter is filled with a mixture of butane and argon and operates in the Geiger region. The shielding is made of 6 cm of boron-loaded paraffin and of 20 cm of lead.

The charge from the anode of the proportional counter is amplified by an FET charge–sensitive preamplifier. The gate of the field effect transistor is directly coupled to the anode. The negative high voltage is connected to the cathode. The preamplifier input noise is about 250 e RMS. Signals from the preamplifier are amplified by a non-overloading amplifier with integrated circuits. The pulses are formed by a pulse shaping network consisting of a single RC differentiation and a double RC integration; the time constants in both cases are 1.8 μsec. The amplifier output is connected to a single channel analyzer which defines the upper and lower limits of the amplitude of signals. The output pulses from the single channel analyzer as well as the pulses from the Geiger guard counters are led to an anticoincidence circuit. Non-coincident pulses from the proportional counter are counted on a slow scaler. The number of pulses registered by the scaler is printed out on a strip printer every 20 minutes to make the statistical processing possible. The total number of pulses is registered in every tenth printout giving the information on the background counting rate. The data thus obtained are processed on the CAE 90-40 computer. The age of samples, the standard deviations of measurements based on the Poisson distribution as well as the best estimate of the true variance are calculated.

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SAMPLE DESCRIPTIONS

A series of measurements of samples of carbon, recent wood, and NBS oxalic acid was performed to check the reliability of the system. Tables 1 and 2 show the results.

While the results for modern wood and NBS oxalic acid were in good agreement when properly corrected, the background count was different for natural old methane (8.53 $\pm$ 0.08) and anthracite (8.89 $\pm$ 0.08). The increase of counting rate was presumably due to tritium contamination during methane synthesis. This was proven in the following way: old natural methane was burnt into CO_2 and CO_2 converted back to CH_4 by applying the standard procedure. The resulting counting rate was higher and close to that of anthracite indicating that

TABLE 1

Measurement of NBS oxalic acid standard. Two samples were prepared from the same batch of oxalic acid.

Sample	Date	Counting rate, cpm
Z-139/I	Feb. 27, 1970	20.89 ± 0.16
Z-139/II	March 3, 1970	21.31 ± 0.14
Z-139/I	March 8, 1970	20.83 ± 0.17
Z-139/II	March 9, 1970	21.16 ± 0.17
Z-139/II	March 10, 1970	21.30 ± 0.16
Z-139/I	March 12, 1970	21.10 ± 0.15
Z-139/II	March 15, 1970	21.33 ± 0.17
Z-139/I	March 18, 1970	21.14 ± 0.15
Z-139/I	March 24, 1970	21.06 ± 0.19
Z-139/II	April 22, 1970	21.08 ± 0.12

TABLE 2

Background counting rate

Sample	Date	Counting rate, cpm
Methane*	Feb. 26, 1970	8.54 ± 0.09
	March 2, 1970	8.58 ± 0.08
Coke	March 1, 1970	9.20 ± 0.1
	April 15, 1970	8.82 ± 0.06
Anthracite	March 7, 1970	9.01 ± 0.09
	March 14, 1970	9.27 ± 0.08
	April 2, 1970	9.11 ± 0.1
	April 13, 1970	9.08 ± 0.06
	April 27, 1970	8.83 ± 0.06
	May 12, 1970	8.89 ± 0.08
Marble	March 6, 1970	9.61 ± 0.09
	March 18, 1970	9.79 ± 0.1

* Natural gas obtained from oil deposits near Stružec, Yugoslavia.

hydrogen used for the methane synthesis was the source of contamination. This assumption was confirmed when a new cylinder of hydrogen was used for methane synthesis (tritium-free hydrogen, Griesheim, Germany). No discrepancy was observed between anthracite and old natural methane counting rates when tritium-free hydrogen was used.

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CHECK SAMPLES

TABLE 3

Check samples

Sample	Age, years B.P.*	Our measurement, years B.P.
UW-147. Subm. by A. W. Fairhall	12,600 ± 150	12,700 ± 200
Hv-2637. Subm. by M. A. Geyh	7735 ± 70	7860 ± 150
Z-114. Measured by Ingrid Olsson, Uppsala, Sweden	150 ± 50	95 ± 50
Z-111. Measured by L. Engstrand, Stockholm	910 ± 100	910 ± 100
Sequoia tree rings**	1080 –1100 B.C.	2920 ± 120 970 B.C.

* Measured by authors listed in Col. 1.

** Age based on tree-ring chronology. Radiocarbon age is ca. 110 yr younger according to observations of other authors (Suess, 1967).

III. ARCHAEOLOGIC SAMPLES

Samples were collected in various places of archaeologic interest in NW Croatia (Zagreb, Varaždin) and along the Adriatic Littoral (Zadar, Nin), Serbia (Lepenski vir) and Macedonia (Stobi). Most of the settlements were inhabitated by Illyrian tribes, followed by Romans and Slavs.

910 ± 100

Z-111. Nin **A.D. 1040**

Wood from ship found from 180 to 200 cm depth in the sea, under 40 cm thick sandy layer, ca. 200 m off coast, at site Ždrijac (44° 14′ N Lat, 12° 52′ E Long). Sample coll. 1966 by Z. Brusić, Archaeologic Collection, Nin.

802 ± 94

Z-124. Nin **A.D. 1148**

Fragment of beam, probably from ship, found in port of Nin (44° 14′ N Lat, 12° 52′ E Long). Sample buried in mud, at 1 m depth, from hole dug out by the dredge during excavation of silt from sea bottom in the port. Sample coll. 1969 by K. Radulić, Inst. for Preservation of Cultural Monuments, Zadar.

Z-129. Zaton near Nin **2063 ± 67**
113 B.C.

Fragment of wooden beam, at 1.80 m depth, in 40 cm thick sandy layer. Coll. 1967, by Z. Brusić.

Z-110. Nin **767 ± 74**
A.D. 1173

Wood from stake of palisade in port of Nin. Coll. 1967 by Z. Brusić.

Z-114. Budva **95 ± 50**
A.D. 1855

Wood from ship, found in sand, Budva (42° 17′ N Lat, 16° 30′ E Long) in 1966. Hulk of ship completely buried in sand except for a few ribs. Measurements indicate remains of a ship of recent historic dating. Coll. 1966 by V. Stanišić, Budva.

Z-115. Lepenski vir **6984 ± 94**
5034 B.C.

Remains of rafter from House 54, Neolithic settlement, Lepenski vir I (44° 38′ N Lat, 20° 16′ E Long). Settlement excavated during construction of a hydro-electric power plant, Djerdap. Sample coll. 1968 by Z. Letica, Fac. of Arts, Belgrade.

Z-143. Lepenski vir **7300 ± 124**
5350 B.C.

Charcoal from Corner A of House 54, Neolithic settlement, Lepenski vir I. Coll. 1969 by Z. Letica.

Z-95. Sisak **1850 ± 150**
A.D. 100

Wood from Roman fortification, near Sisak (45° 28′ N Lat, 14° 02′ E Long). Coll. 1967 by S. Vrbanović, Mus., Sisak.

Z-132. Varaždinske toplice **1900 ± 150**
50 B.C.

Fragments of wood (probably remains of rafter from house) dug out at site of wooden dwellings of early imperial settlement Aquae Iasae, Roman Empire (46° 14′ N Lat, 14° 05′ E Long). Locality is high in moisture and swampy ground. Archaeologic evidence confirms same environmental features in early times. Upper layers are heavy humus followed by clay and loam underlain by larger or smaller amount of rotten matter, or various streaks of sand and marl. Coll. 1967 by M. Gorenc and B. Vikić, Archaeologic Mus., Zagreb.

Z-146. Sčitarjevo **2011 ± 80**
61 B.C.

Early imperial layer submerged in ancient times. Grain found at 1 m depth during sounding in Roman municipality Andautonia in vicinity of Zagreb. Sample coll. 1969 by M. Gorenc.

Z-144. Stobi **1750 ± 180**
A.D. 200

Charcoal from remains of fire destroyed settlement Stobi (41° 32′

N Lat, 21° 51′ E Long). Sample from a layer of ash and charcoal found during excavation of ancient theatre, Stobi. Layer of ash and charcoal spreads along entire cross section of fire area. Coll. 1969 by N. and D. Srdoč.

830 ± 103

Z-142. Zagreb **A.D. 1120**

Wood of rafter, depth 2 m, in medieval layer (45° 48′ N Lat, 13° 38′ E Long). Probably from foundation of former Capuchin convent in the Upper Town. Coll. 1969 by I. Šarić, Regional Inst. for Preservation of Cultural Monuments.

37,400 ± 640

Z-134. Velika Pecina **35,450 B.C.**

Charcoal from fireplace, found in a cave, Ravna Gora, NW dist. of Croatia (46° 17′ N Lat, 16° 2′ E Long, height 428 m).

IV. GEOLOGIC SAMPLES

1200 ± 100

Z-135. Dabar near Otočac **A.D. 750**

Sub-fossil wood that started to emerge at the bank of a peat bog in 1965. Coll. 1966 by I. Horvat, Fac. of Forestry, Zagreb.

896 ± 94

Z-147. Oroslavje **A.D. 750**

Wood emerging from steep bank of stream Topličina. Coll. 1969 by A. Sliepčevič.

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