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THE RADIOCARBON LABORATORY AT THE UNIVERSITY OF BARCELONA

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INTRODUCTION

In 1983, the University of Barcelona, the Institut d'Estudis Catalans and the Department of Culture of the Generalitat de Catalunya agreed to establish a laboratory for radiocarbon measurement at the Analytical Chemistry Department of the University of Barcelona. The liquid scintillation technique was chosen for radiocarbon counting. The counting laboratory is in the basement of a six-story building.

In 1985, the laboratory started its measurements in the dating and environmental fields. The procedures for benzene synthesis and for counting have been improved continuously since then, and current procedures are outlined in the experimental part of this paper. We consider these procedures an important aspect of laboratory quality-control techniques. In the last decade, quality assurance in measurements received special consideration, and radiocarbon laboratories have been very interested in this topic (Scott, Long & Kra 1990; Long 1990). One of the activities related to quality assurance is quality control, which is defined as an overall system of activities that guarantees that a service meets the needs of the users (Taylor 1987). Specific operating procedures (SOP) are one of the basic elements of quality control, and their publication allows them to be criticized, so that laboratories can improve their quality.

Quality assurance consists of two separate activities: quality control and quality assessment. Quality assessment techniques involve internal test samples, external reference materials, standard reference materials and collaborative tests, among others. We present here the results, for samples supplied by the radiocarbon laboratory of Lyon, considered as external reference materials, as well as the results found in two intercomparison exercises, the International Collaborative Study organized by Glasgow University, and an intercomparison study organized by the Iberian radiocarbon dating laboratories.

For the first samples, activity correction for ^{13}C fractionation has only been applied to the contemporary standard. The recent setting up of a mass spectrometry laboratory in the Analytical Chemistry Department now allows $\delta^{13}C$ correction to be applied to all dating samples.

MATERIAL AND METHODS

Treatment of Samples

Sample preparation is preceded by careful visual separation and hand removal of gross impurities.

Charcoal and wood are successively pretreated with 2M HCl at 90°C for 24 hours, with 0.1M $Na_4P_2O_7$ for 24 hours at room temperature, and finally with boiling 0.5M HCl for 20 minutes.

Bones are pretreated according to Longin's (1971) procedure, except in two aspects. The sedimentation time after initial acid attack is longer (1 hour) in order to attain better sedimentation, and the possibility of a premature collagen hydrolysis is monitored every 20 minutes by the biuret reaction. Also, hydrolysis of bone collagen is carried out in a 0.01M H_3PO_4/KH_2PO_4 buffer medium at pH 2.8 and 90°C. In this way, hydrolysis is accomplished in only one 18-hour run. The colloidal solution containing bone gelatin is dried with a rotating evaporator.

Shells. In order to eliminate adhered organic matter and superficial carbonate layers, shells are treated with 6% H_2O_2 for 10 minutes in an ultrasonic bath at room temperature. Then 2M HCl is added to make a 0.1M HCl solution. When bubbling has stopped, shells are washed with distilled water and the treatment is repeated until the weight loss is about 12% (Mangerud & Gulliksen 1975).

Peats and sediments are treated only with 2M HCl at 90°C for 24 hours.

Benzene Synthesis

Installation for benzene synthesis (Garcia 1989) is schematically shown in Figure 1. There are two vacuum lines, each one connected to its own two-stage rotary vacuum pump (BV1 and BV2), model E2M18, from EDWARDS.

The installation has a PHONON unit (PU), model 400, for the combustion of materials with high carbon content. Materials with low carbon content are combusted in a tube (CT) with a CuO packing heated at 800°C with a tubular electrical furnace (Fig 2). Carbonates are decomposed in the reaction flask RF. There is a duplicate system for CO_2 capture and separation from O_2 as well as for benzene synthesis from CO_2. The vacuum level is monitored by two Pirani gauges (P1, P2), model PRL10, connected to a controller, model 1001, from EDWARDS. The gas pressure at different points of the installation is measured with three Bourdon gauges (M2, M3, M3′) and five mercury manometers (M4, M5, M5′, M6, M6′).

Moisture separation is achieved by cryogenic traps T1, T2, T2, T3, T7, T9, T7′ and T9′ by means of a mixture of liquid nitrogen and alcohol at −80°C.

Separation of CO_2 from O_2 in combustion gases is carried out by capture in traps (T4, T5, T6 or T4′, T5′, T6′) by means of liquid nitrogen and working at a pressure (checked with gauges M3 or M3′) lower than the vapor pressure of liquid oxygen at the temperature of the liquid nitrogen (120 torr). In order to eliminate the last traces of moisture contained in carbon dioxide or acetylene, the gas captured in coil traps T6, T6′, T12 and T12′ is carried back to previous traps, and coil traps are immersed in the cryogenic mixture for water.

Carbon dioxide is stored in reservoirs D1–D6 for long-term storage for radon decay, and in reservoirs D7 and D7′ for short storage before reduction. Acetylene is stored in reservoirs D8 and D8′ before trimerization to benzene.

CO_2 samples for $\delta^{13}C$ measurement are taken through valve C22.

CO_2 Preparation

1. *From oxalic acid contemporary standard* – 25g of oxalic acid is weighed and put into the reaction flask RF together with a magnetic stirrer. Funnel F containing 350ml of 0.45M H_2SO_4 solution, prepared by dilution with previously boiled distilled water, is placed in site and the system between RF and valve C14 is evacuated. When a stable vacuum level is attained, with water-capture traps immersed in their cryogenic mixture, valve C8 is closed, nearly all the acid solution is poured onto the oxalic acid, and the mixture is magnetically stirred to dissolve as much oxalic acid as possible.

Dynamic vacuum is stopped, CO_2-capture traps T4–T6 are immersed in liquid nitrogen and 300ml of 5% $KMnO_4$ solution, prepared with previously boiled distilled water, is put in the funnel stoppered with a soda lime tower. About 20% of the permanganate solution is poured into the reaction flask and when the solution becomes colorless, successive small portions of permanganate solution are added as the previous portion is decolored. During addition of the permanganate solution, care must be taken that pressure measured in gauge M2 does not exceed 660 torr. When

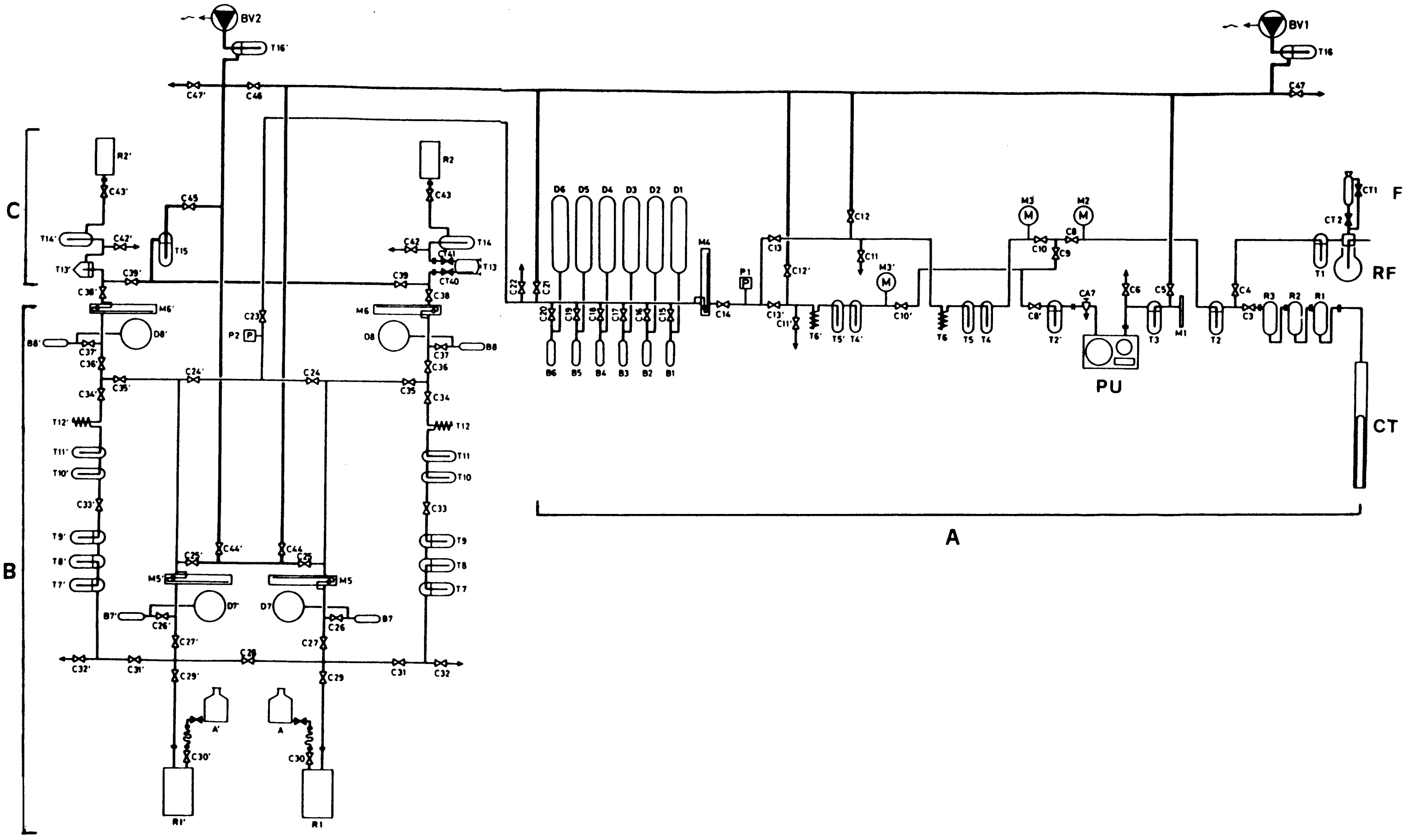

Fig 1. Installation for benzene synthesis
A – CO_2 preparation
B – Acetylene preparation
C – Benzene preparation

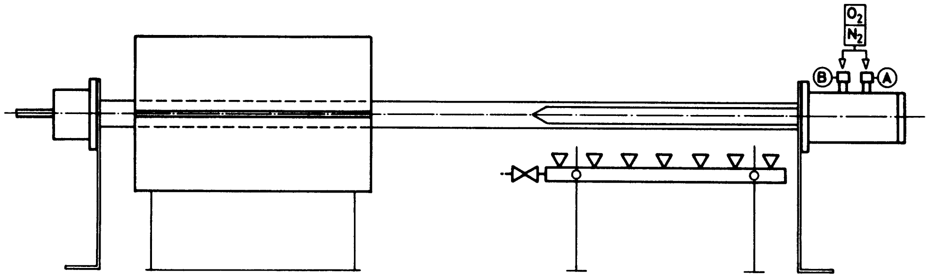

Fig 2. Combustion system for materials with low carbon content.

this pressure is reached, addition is stopped, and valve C8 is opened carefully to allow CO_2 to be captured in its traps until bubbling of the solution becomes violent. The additions are repeated until a permanent dark brown precipitate appears. At this point, the reaction is finished, valve C8 is again opened to allow capture of CO_2. In order to recover the last traces of the gas, the complete system is reconnected to dynamic vacuum, and care is taken to avoid violent bubbling. Finally, CO_2 is dried through coil trap T6 and transferred to a storage reservoir D1–D6.

2. *From materials with low carbon content* – the combustion tube is used for this kind of material. The sample is placed in the inner tube and washing flasks R1–R3 are filled with slightly acidic saturated potassium permanganate solution. The system from TC to C13 is simultaneously purged with a current of oxygen through the inner tube and a current of nitrogen through the outer tube. After purge, dynamic vacuum is connected, flow is regulated in such a way that pressure in the combustion tube is about 600 torr, and pressure in CO_2 traps T4′-T6′ is lower than 120 torr. Finally, CO_2 traps are immersed in liquid nitrogen and gas burners are ignited. When combustion is complete, trapped CO_2 is dried and transferred to one of the storage reservoirs D1–D6. Occasionally, combustion is preceded by pirolysis, passing a current of oxygen through the outer tube and a current of nitrogen through the inner tube.

3. *From materials with high carbon content* – the Phonon combus unit is used according to its directions. After combustion, the CO_2 is purified, trapped and stored as described above.

4. *From carbonate materials* – The sample is placed in the reaction flask RF and the system from RF to C13 is evacuated. Once the vacuum level is stable, water traps T1 and T2 are immersed in their cryogenic mixture and dynamic vacuum is stopped in C8. Cold, previously boiled distilled water is poured from funnel F onto the sample covering it. Carbon dioxide traps are immersed in liquid nitrogen, and an excess of 1:1 phosphoric acid is put in the funnel and poured slowly into the reaction flask. When pressure, checked in gauge M2, reaches 700 torr, acid addition is stopped and valve C8 is carefully opened to allow CO_2 to be captured in its traps until bubbling of the solution becomes violent. Acid addition is continued and this procedure is repeated until the attack is complete. The procedure then followed is the same as that described for oxalic acid oxidation.

Preparation of Acetylene

Reduction of carbon dioxide to acetylene is carried out in refractory stainless steel reactors R1 or R1′ heated in electrical furnaces. A 30% excess of metallic lithium over the stoichiometric amount required is put in the reactor, which is then evacuated and heated to 650°C. Afterwards, dynamic vacuum is stopped, and CO_2, previously transferred to reservoirs D7 or D7′, is allowed to expand slowly in the reactor. When the CO_2 pressure has decreased to a very low value, the furnace is heated to 800°C. Once pressure is no longer measurable with the mercury manometer, dynamic vacuum is applied for 1 hour to ensure effective radon removal. Reactors are left to attain room temperature, water traps T7 and T9 are immersed in their cryogenic mixture, trap T8 is filled with syrupous phosphoric acid for ammonia removal, and traps are evacuated to a stable level. Traps T10–T12 are sunk in liquid nitrogen, dynamic vacuum is stopped, and an excess of low-tritium water (< 2.2 Bq/l) is carefully poured into their respective reactors. Hydrogen produced by the excess of lithium is allowed to expand in reservoir D7. When nearly all the water has been poured in, dynamic vacuum is carefully connected to the reactor to avoid violent boiling. Finally, the collected acetylene is dried and transferred to reservoir D8. The yield of acetylene is usually about 95%.

Benzene Preparation

Benzene is obtained by catalytic trimerization of acetylene with catalyzer PKN from Kalichemie Iberia (Von Pietig & Scharpenseel 1966) placed in 300cm^3 glass tubes heated in tubular electrical furnaces. The catalysis tube filled with the catalyzer is heated to and kept at 400°C for 30 minutes in open air. It is then connected to line and kept at the same temperature for 2.5 hours under dynamic vacuum. After heating, the catalyzer is cooled to 60°C, dynamic vacuum is stopped and acetylene is allowed to expand into the catalyzer. Once the pressure has attained about 120 torr, valve catalysis tube C43 is closed, residual acetylene is collected in trap T14 with liquid nitrogen and, in order to increase residual gas pressure, valve C37 is closed. Residual acetylene is allowed to sublimate back to the catalyst. When residual acetylene pressure becomes stable, trap T13 is immersed in the cryogenic mixture at –80°C and the tubular furnace is heated at 170°C for at least 1 hour. System from R2 to C36 is carefully connected to dynamic vacuum until the pressure is not measurable. Dynamic vacuum is then stopped, the cryogenic mixture is replaced by liquid nitrogen and dynamic vacuum is applied again for 30 minutes to remove all benzene from the catalyst. The benzene yield is about 95%.

Measurement of the Activity

Apparatus

1. *Counters* – The Laboratory has two liquid scintillation counters: an LKB-Wallac Rackbeta 1217 Kangaroo and a Packard TriCarb 2000 CA/LL. The characteristics of the first counter are: high voltage stabilization circuit "high-low" coincidence bias selection, linear amplification and a spectrum display of 256 logarithmic channels (1-2800 KeV range), four independent channels with variable windows for data accumulation, automatic external ^{226}Ra source for quenching monitoring and refrigeration. The characteristics of the second counter are: linear amplification MCA of 4096 channels (SPECTRALYZER™, 1-2000 KeV range), a background discriminator from sample decay based on the SPECTRALYZER™ three-dimensional spectrum analyzer, three independent regions with variable thresholds for data accumulation, automatic external standard ^{133}Ba source, spectrum storage facility and refrigeration.

2. *Vials* – Two kinds of vials are used – 7ml teflon-copper vials from LKB-Wallac, modified to diminish vapor loss (Rauret, Mestres & García 1988), and 20ml low potassium borosilicate glass vials from Packard, modified in the same way by replacing the original foil lined seal by a rubber-teflon seal (J Evin, pers commun) and by adding a viton O-ring on the neck base.

Every teflon-copper vial and glass vial presents different values of the quenching parameter when counted with blank solutions (Rauret, Mestres & García 1988, 1990). These different values of the quenching parameter, due to an intrinsic quenching effect of the vials, are measured in the counting conditions, recorded, and vials are ranked accordingly.

Copper-teflon vials are cleaned according to the following procedure: immediately after use they are washed with blank benzene, then filled with benzene, and the benzene is changed twice over a two week period. After treatment with benzene, vials are washed with hexane and dried under vacuum in a desiccator at 50°C for 4 hours using a trap immersed in liquid nitrogen between desiccator and water pump. Vials are filled again with benzene, left to stand overnight, and dried again under vacuum in the same way.

Glass vials are cleaned immediately after use by washing with benzene and hexane.

Counting Conditions

Counting solutions are prepared according to the following procedure: 3.6ml of synthesized benzene are weighed in a previously tared vial and then 0.4ml of 5% Bu-PBD solution in inactive benzene is added; if the amount of synthesized benzene is less than 3.6ml, all the obtained benzene is weighed in the previously tared vial, its volume is calculated using its specific gravity and the quantity required to make up 3.6ml is added as inactive benzene and weighted. Blanks for background measurement are prepared in the same way, using inactive benzene. Weight before and after counting is recorded to evaluate any excessive evaporation during counting time. This procedure was established previously (Rauret, Mestres and García 1989).

This procedure does not guarantee a constant efficiency counting for two reasons: the first is that, although the chemical composition of counting solutions is accurately known, it is not rigorously constant due to the habitual imprecision in measuring small volumes; the second reason is the intrinsic quenching effect of the vials. In order to reach the accuracy that radiocarbon dating requires, possible small variations in counting efficiency must be eliminated or reduced by correction. This correction is carried out by calculating the count rate corresponding to a 100% counting efficiency by means of an experimental correlation curve between counting efficiency and quenching parameter. Corrected count rate to 100% counting efficiency and referred to 1g of benzene derived from the sample is referred to here as normalized count rate (see Calculations, below).

Instruments – The first channel of the LKB counter is used for measuring ^{14}C; its window is selected using a teflon-copper vial whose intrinsic quenching parameter has a central value in its rank. The select window furnishes the maximum figure of merit E^2/B, but the lower threshold has been shifted to higher energies to avoid the interference of tritium coming from the water used for the lithium carbide hydrolysis. The second channel is used for disclosing the possible presence of radon. The low threshold of the window is set immediately after the end of the ^{14}C spectrum. The 3rd and 4th channels are used for quenching measurement by the external standard channel ratio (ESR) method: the 3rd channel contains the wide window and the 4th contains the narrow window; the lower threshold is the same for both windows. The ESR parameter is defined as count rate in narrow window/count rate in a wide window. To attain maximum sensitivity in efficiency correction, window thresholds are selected for producing maximum variation of ESR parameter between two differently quenched solutions.

Two channels of the Packard counter are used, one for ^{14}C measurement and the other for radon control. The selection criteria for the window thresholds are the same as those used for the LKB counter. The parameter for quenching measurement, t-SIE, is used, which is included in the software package of the instrument and available on request.

Correlation Curve Between Efficiency and Quenching

1. *Stock solutions* – a) Activity standard solution. To a previously tared hermetic glass bottle, 80ml of MERCK GR benzene are added and weighed. The contents of a vial of a certified 1.136 × 10^6 dpm/g standard of ^{14}C-labeled toluene from Amersham is then poured into the bottle and weighed again. In another previously tared glass bottle, 80ml of the same benzene is added and weighed, and then 5ml of the former solution is also added and weighed. In this way, an activity standard solution of 3698 dpm/g of ^{14}C with a content of 0.32% of toluene is obtained; b) 5% Bu-PBD solution in MERCK GR benzene; c) 1% and 2% (v/v) CCl_4 solutions in benzene, as chemical quencher.

2. *Preparation and counting of efficiency standards* – Twelve vials filled with 4ml of different quenched solutions are used for each counter. The vials with maximum and minimum intrinsic quenching are not quenched at all and the higher their intrinsic quenching effect, the more the others are quenched chemically.

Each vial is added to as follows: an adjustable pipette with intervals of 0.01ml is used to add inactive benzene and 1 or 2% CCl_4 solution to each vial in such a way that the sum is 1ml and CCl_4 content in the final solution ranges from 0.03 to 0.3% at increments of 0.03%. Then, 0.4ml of Bu-PBD solution is added and vials are stopped and weighed. Finally, 2.6ml of standard activity solution is added to each vial and the vials are definitively stoppered and weighed again. In this way, the activity of each vial is accurately known.

The series of solutions are counted for 100 minutes divided into 10-minute intervals. For each interval, the count rate and the measured quenching parameter are printed out. Efficiency of each solution is correlated with the mean value of the obtained quenching parameters by means of a 2nd- or 3rd-degree polynomial regression.

Counting protocol. Modified vials improve their sealing with respect to non-modified vials. However, for long counting protocols and, especially for long-term storage of counting solutions of contemporary standard, it is not enough. Thus, long counting protocols with sequences of several samples, blanks and modern standards are not used; each solution is counted in a run. For the same reason, continuous counting of the modern standard is not possible. Thus, the outlined experimental counting procedure allows the determination of the normalized count rate of the sample as well as the normalized count rate of the modern standard. For age determination, however, the normalized count rate of benzene derived from samples is measured using the same counter and the same correlation curve between efficiency and quenching parameter as those used for measurement of the normalized count rate of the modern standard to which the sample is referred.

Counting is carried out continuously but is divided into intervals of the same duration. This procedure allows for the detection of deviations or any dispersion in counting results other than those expected from the natural dispersion of radioactive decay. In order to assess these effects, the ratio between the Poisson standard deviation and the experimental standard deviation is calculated. This ratio, referred to here as counting quality parameter (see Calculations, below), must be close to 1, if counting is regular.

Blanks for background control are counted for a 12-hour period divided into 1-hour intervals. The count rate and the value of quenching parameter are printed out for each interval. Background and mean value of quenching parameter associated with each vial are recorded and outliers are rejected. If an outlier is obtained, the vial is rewashed, a new blank is prepared and it is recounted. Samples and contemporary standards are counted for 36 hours in 30 intervals of 72 minutes. Count rate and value of quenching parameter is printed out for each interval.

In order to assess possible short-term variations in the background level, blank counting is alternated with sample counting. Also, a sealed blank is counted weekly.

Calculations. The LKB counter can give counting results as accumulated counts and count rate. Since count rate is given with a low precision of only 0.1, accumulated counts are used for calculations. The Packard counter, however, can give counting results only as count rate but its precision can be defined by the user.

Definition of Symbols

c_j	accumulated counts in the j-th counting interval
c	mean value of the accumulated counts in each one of the intervals
C_j	count rate measured in the j-th counting interval
C	count rate corresponding to total counting time
t	duration of a counting interval
n	number of intervals in total counting time
var_t	Poisson variance referred to the total counting time
var_i	Poisson variance referred to the counting interval
var_e	experimental variance
var	unspecified variance
r	counting quality parameter
x_j	value of the quenching parameter obtained in the j-th interval
E_j	value of the efficiency, expressed as a fraction, corresponding to x_j through the experimental correlation curve between efficiency and quenching parameter
E	value of the efficiency, expressed as a fraction, associated with a solution
B	background
R	net count rate
a	weight of counted synthesized benzene
f	activity correction factor to −25‰ wrt PDB ^{13}C fractionation
A	normalized count rate
A_N	normalized count rate corrected to −25‰ wrt PDB ^{13}C fractionation
A_{0N}	present normalized count rate corresponding to the absolute international standard activity, A_{abs}. These magnitudes are related as follows (Stuiver & Polach 1977): $$A_{0N} = A_{abs} \exp[-\lambda(p - 1950)],$$ where p denotes the present year
A_{sN}	normalized count rate of benzene derived from sample, corrected to −25‰ wrt PDB ^{13}C fractionation
$t_{½}$	Libby's ^{14}C half-life of 5568 years.

Count-Rate Calculations

LKB counter

$$c = (1/n) \Sigma c_j$$

$$C = c/t$$

$$var_t(C) = C/nt$$

$$var_i(c) = c$$

$$var_e(c) = [1/(n - 1)] \Sigma (c - c_j)^2$$

$$r = [var_i(c)/var_e(c)]^{1/2}$$

Packard counter

$$\begin{aligned}
C &= (1/n)\ \Sigma\ C_j \\
\mathrm{var}_t(C) &= C/nt \\
\mathrm{var}_i(C) &= C/t \\
\mathrm{var}_e(C) &= [1/(n-1)]\ \Sigma\ (C - C_j)^2 \\
r &= [\mathrm{var}_i(C)/\mathrm{var}_e(C)]^{1/2}
\end{aligned}$$

Efficiency calculations

$$\begin{aligned}
E_j &= f(x_j) \\
E &= (1/n)\ \Sigma\ E_j \\
\mathrm{var}_e(E) &= [1/(n-1)]\ \Sigma\ (E - E_j)^2
\end{aligned}$$

Net count rate calculations

$$\begin{aligned}
R &= C - B \\
\mathrm{var}(R) &= \mathrm{var}_t(C) + \mathrm{var}_t(B)
\end{aligned}$$

The count rate corresponding to the most recent blank measured in the same vial is taken as background for each counting.

Calculation of the normalized count rate

$$A = R/Ea$$

Taking into account that both samples and new NBS international standard reference oxalic acid must be corrected for ^{13}C fractionation to −25‰ with respect to PDB, corrected normalized count rate is calculated according to

$$\begin{aligned}
f &= 1 - 2(25 + \delta^{13}C)/1000 \\
A_N &= fA \\
\mathrm{var}(A_N) &= A_N^2[\mathrm{var}(R)/R^2 + \mathrm{var}_e(E)/E^2]
\end{aligned}$$

Measurement and calculation of the present normalized count rate corresponding to the absolute international standard activity. The normalized count rate corrected by ^{13}C fractionation of at least two samples of benzene derived from new NBS oxalic acid is measured. If the difference between the experimentally obtained values, A_{1N} and A_{2N}, is not significant, the weighted mean and its variance are calculated according to the following equations:

$$\begin{aligned}
A_N &= [A_{1N}/\mathrm{var}(A_{1N}) + A_{2N}/\mathrm{var}(A_{2N})] \ / \ [1/\mathrm{var}(A_{1N}) + 1/\mathrm{var}(A_{2N})] \\
1/\mathrm{var}(A_N) &= 1/\mathrm{var}(A_{1N}) + \mathrm{var}(A_{2N})
\end{aligned}$$

Then, the present normalized count rate corresponding to the absolute international standard activity and its variance are calculated thus:

$$\begin{aligned}
A_{0N} &= 0.7459\ A_N \\
\mathrm{var}(A_{0N}) &= (0.7459)^2\ \mathrm{var}(A_N)
\end{aligned}$$

The present normalized count rate corresponding to the international standard activity is measured at least once a year for each counter, and each time, a new correlation curve between efficiency and quenching parameter is obtained.

Age calculations. ^{14}C age and its variance are given by

$$t = (t_{½}/\ln 2)\ \ln(A_{0N}/A_{sN})$$
$$\mathrm{var}(t) = (T_{½}/\ln 2)^2[\mathrm{var}(A_{0N})/A_{0N}^2 + \mathrm{var}(A_{sN})/A_{sN}^2].$$

Obviously, as has been stated above, the values of A_{0N} and A_{sN} are determined with the same counter and with the same efficiency - quenching parameter correlation curve.

Quality Assessment

1. *Activity Measurements*

a. *Short-term controls.* An internal-test active solution prepared according to the method described above, with an activity similar to the absolute international specific activity is prepared by dilution of the 3698 dpm/g solution. The normalized count rate of samples of this solution, considered as a measure of the specific activity of the internal-test samples, are measured every month, and results plotted as a cusum chart, taking as a target value the specific activity of the active solution. Any abnormal deviation of the cusum would indicate a performance failure of the counter.

TABLE 1
Results of the first stage of the International Collaborative Study

Sample Identifier	Age of Sample	Average	Range
13 S	800 ± 40		
13 K	910 ± 45	930	1300
13 B	6730 ± 60		
13 H	6770 ± 60	6900	1700

TABLE 2
Results of the measurement of an active solution
by the Iberian Radiocarbon Laboratories

Laboratory	Value of f
UGRA*	0.595 ± 0.002
ICEN**	0.586 ± 0.002
UBAR†	0.588 ± 0.006

*University of Granada (Spain)
**Institute of Science and Nuclear Engineering, LNETI (Portugal)
†University of Barcelona (Spain)

TABLE 3
Interlaboratory check samples

Reference date	UBAR date
Ly-2388 3150 ± 100 BP	UBAR-2 3210 ± 90 BP
Ly-2589 790 ± 100 BP	UBAR-3 765 ± 80 BP

b. *Long-term controls.* Good agreement between normalized count rates corresponding to the absolute international standard activity, measured both with the same and different counters, is further indication of good performance.

c. *Intercomparison samples.* The Laboratory has participated in the International Collaborative Study organized by the University of Glasgow (Scott, Long & Kra 1990) and has promoted an interlaboratory study between the other Iberian radiocarbon laboratories. Stage 1 of the International Collaborative Study focused on the counting process only. Our results, referred to a modern activity standard uncorrected by isotopic fractionation, are shown in Table 1. Moreover, the Laboratory has sent a sample of the internal-test solution to the other Iberian radiocarbon laboratories for measurement. Table 2 shows the results of these measurements, expressed as the ratio, $f = A_{0N}/A$.

2. *Global Process*

Two charcoal samples, furnished by Jacques Evin, Centre de Datations et d'Analyses Isotopiques, Claude Bernard University of Lyon, were dated. Table 3 shows the results obtained by our laboratory (UBAR), referred to a modern activity standard uncorrected by ^{13}C fractionation.

Stage 2 of the International Collaborative Study has involved synthesis and counting, and Stage 3, pretreatment, synthesis and counting. Table 4 shows our results, together with some characteristics of the samples.

TABLE 4

Results of Stages 2 and 3 of the International Collaborative Study (Scott, pers commun 1989)

Stage	Sample material & identifier	Absolute age (AD/BC)	Equivalent ^{14}C date (BP)	Average of ICS (BP)	Range	UBAR dates (BP)
2	Cellulose 13-I	241-260	2160-2220	2250	1900	2080 ± 60
2	Cellulose 13-S	Replicate of sample above				2240 ± 50
2	Algal 13-R	--	--	2120	1800	2060 ± 50
2	Algal 13-W	Replicate of sample above				2080 ± 50
3	Wood 13-U	221-240 BC	2185	2207	--	2270 ± 70
3	Wood 13-V	Replicate of sample above				2290 ± 70
3	Wood 13-A	AD 1841-1870	~100	111	--	80 ± 60
3	Wood 13-X	AD 1521-1550	~290	297	--	310 ± 60
3	Peat 13-T	--	--	3338	--	3150 ± 90
3	Peat 13-Z	Replicate of sample above				3490 ± 70
3	Shell 13-P	--	--	637	--	790 ± 60
3	Shell 13-Y	Replicate of sample above			--	730 ± 60

The Iberian Radiocarbon Laboratories have dated 4 samples, 3 of charcoal and 1 of wood. Each laboratory has carried out the complete process, pretreatment, synthesis and counting. Table 5 shows results.

TABLE 5
Results obtained (yr BP) for Iberian interlaboratory check samples

Sample material	CSIC*	UGRA	ICEN	UBAR
Charcoal	3600 ± 50	3680 ± 80	3850 ± 35	3640 ± 50
Charcoal	2520 ± 50	2530 ± 80	2640 ± 80	2650 ± 90
Charcoal	2880 ± 40	3030 ± 80	--	2910 ± 90
Wood	1920 ± 40	2020 ± 80	1990 ± 35	2040 ± 100

*Consejo Superior de Investigaciones Cientificas, Madrid (Spain)

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