

## COMPUTER ANALYSIS AND INTERPRETATION OF RADIOCARBON DATA

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Abstract

Following factors influencing accuracy of radiocarbon results have been considered:  $^{14}\text{C}$  half-life, variations of  $^{14}\text{C}$  concentration over last 40,000 years, isotope fractionation, initial  $^{14}\text{C}$  concentration, contamination due to man activities (fossil fuel combustion, nuclear explosions), standard (oxalic acid) measurement error, barometric and temperature effects, the amount of collected sample and the precision of measuring technique.

A review of various modes of  $^{14}\text{C}$  result representation has been presented (conventional  $^{14}\text{C}$  age, percent modern, depletion or enrichment wrt. standard and  $\delta^{13}\text{C}$  and dendrochronological correction). A computer output list for radiocarbon results used at Rudjer Bošković Institute with statistical tests enabling a better control of obtained results has been described.

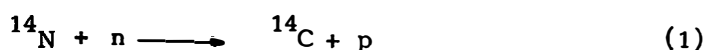
Introduction

Radiocarbon dating method has been successfully applied to various scientific disciplines for more than 30 years (1). The most important data for users of radiocarbon is the accuracy as well as the interpretation of  $^{14}\text{C}$  data.

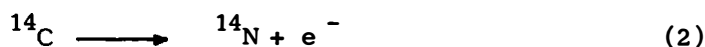
In early years of radiocarbon dating it was considered that the reliability of dating depends only of measurement technique and on the precise determination of  $^{14}\text{C}$  half-life, as well as on the careful sample

collection. Today other factors began to influence precision of a dating result as well.

Method of dating by measuring  $^{14}\text{C}$  isotope activity is based on the fact that the atmospheric carbon dioxide, as well as all organic materials in the biosphere, contains a certain amount of  $^{14}\text{C}$  isotope. Radioactive carbon has origin in high atmospheric layers by interaction of cosmic radiation produced neutrons with nitrogen according to the relation:



Unstable  $^{14}\text{C}$  nucleus decays by emission of  $\beta$ -particles according to:



with half-life of about 5700 years. Radioactive carbon isotope oxidates to carbon dioxide and together with inactive carbon molecules distributes isotropically in the atmosphere, biosphere and hydrosphere. Radiocarbon spreads through feeding chain into the plants by assimilation process and then to animals and human beings. Assuming that the neutron flux has been constant over a period much longer than the half-life of  $^{14}\text{C}$  an equilibrium has been reached, since the  $^{14}\text{C}$  atoms concentration diminishes according to the law of radioactive decay:

$$N = N_0 \exp \left( - \frac{\ln 2 \cdot t}{T_{1/2}} \right) \quad (3)$$

In other words, according to equations (1) and (2), the desintegrated radiocarbon is compensated by newly created radiocarbon in the upper layers of the atmosphere. In eq. (3)  $N_0$  is the initial and  $N$  final number of radiocarbon nuclei and  $T_{1/2}$  is the half-life period. The radiocarbon

concentration in living organisms is equal to the concentration in the atmosphere or hydrosphere. Radiocarbon activity decreases after the death of the organism according to the relation (3) because the replenishment of  $^{14}\text{C}$  atoms is interrupted. By measuring activities  $A$  and  $A_0$  instead of  $N$  and  $N_0$  one can calculate the time elapsed from the death of the organism.

Factors influencing the accuracy of radiocarbon activity measurement are:

- error in  $^{14}\text{C}$  half-life measurement;
- changing of  $^{14}\text{C}$  specific activity over last 50 000 years, as well as geographic variations of  $^{14}\text{C}$  activity;
- isotope fractionation;
- initial concentration of  $^{14}\text{C}$  atoms;
- contamination of samples because of man activities in the atmosphere;
- usage of a reliable standard;
- precision of the measurement technique;
- increasing of uncertainty of the results because of insufficient quantity of sample;
- dependence of measured activity on the atmospheric pressure and temperature.

### Half-life

The method of half-life determination is based on the mass spectrometric analysis of carbon dioxide which contains a relatively great proportion of radioactive isotope  $^{14}\text{C}$  and on the measuring of the specific activity by means of the proportional or Geiger-Müller counter. The best result obtained so far is the mean of the results

obtained in the USA , Great Britain and Sweden in the period 1961-1962. This value is  $5730 \pm 40$  years (2,3,4) and it is different from previously accepted half-life (5570 yr.) by  $\approx 3\%$ . In spite of that , the decision was made at the 5th Radiocarbon Dating Conference (Cambridge , 1962) to report radiocarbon results calculated by using standard Libby half-life (1) which is  $5570 \pm 30$  years to avoid confusion in literature since the earlier results were based on Libby half-life. The ratio between the new half-life (denoted by index "2") and the Libby half-life (index "1") is 1.03. In the following table the comparative values of these two half-life periods are given, as well as the corresponding mean life periods and the desintegration constants :

	$T_{1/2}$	$\tau = T_{1/2} / \ln 2$	$\lambda = 1/\tau$
	year	year	year
1.	5570	8030	$1.245 \cdot 10^{-4}$
2.	5730	8270	$1.209 \cdot 10^{-4}$

#### Radiocarbon variations in the past and distribution in the atmosphere

The variations of radiocarbon concentration in the past have been discovered by comparing the age of samples obtained by radiocarbon method with that obtained by tree-ring counting (dendrochronology). Relatively old samples have been measured for this purpose (Sequoia gigantea , Pinus aristata and others) which enabled a comparison to be made up to 7000 years in the past. A deviation of  $^{14}\text{C}$  concentration in the past has been so discovered. This deviation is significant for samples older than 2000 years. It is necessary to

emphasize that the deviation from the absolute chronological scale is within several percents. Several precise measurements have been published (16) enabling us to take into account variation of  $^{14}\text{C}$  concentration in the past and to correct  $^{14}\text{C}$  data.

The changes in atmospheric radiocarbon concentration can be the consequence of cosmic rays intensity change or the consequence of magnitude of radiocarbon reservoir exchange. The cosmic radiation intensity depends on the magnetic dipole momentum of the Earth and on the intensity of solar winds.

In spite of the anisotropy in neutron flux from geomagnetic equator to the poles, it was established that there are no essential differences in the radiocarbon specific activity in the atmosphere which can be explained as the results of geographic locations. Due to air circulation causing mixing of carbon dioxide in the atmosphere there has not been observed a gradient in radiocarbon concentration in the atmosphere.

#### Isotopic fractionation effect

An error in radiocarbon results is introduced if the number of  $^{14}\text{C}$  atoms in the sample decreases in another way except by radioactive desintegration. The process can be the exchange of carbon atoms in the sample with fossil carbonate such as the limestone or carbon dioxide of magmatic origin or other fossil substances. It is a slow process and occurs by diffusion of atoms (5). If decreasing of  $^{14}\text{C}$  concentration occurs a simultaneous decreasing of  $^{13}\text{C}$  takes place too. One can correct the sample age by measuring the ratio  $^{13}\text{C}/^{12}\text{C}$ . The  $^{13}\text{C}/^{12}\text{C}$  ratio is obtained by mass spectrography. The relative deviation of the ratio  $R = ^{13}\text{C}/^{12}\text{C}$  of stable carbon isotopes in relation to standard Belemnitella americana from Peedee formation, South Carolina, USA (PDB) has been measured according to the relation:

$$\delta^{13}\text{C} = \frac{R_S - R_{\text{PDB}}}{R_{\text{PDB}}} \cdot 1000\% \quad (4)$$

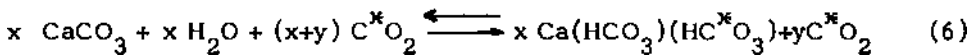
The  $\delta^{13}\text{C}$  age correction has been normalised to the value -25‰ which is the  $\delta^{13}\text{C}$  value of wood:

$$A'_{\text{SN}} = A_{\text{SN}} \left[ 1 - \frac{2 \cdot (25 + \delta^{13}\text{C})}{1000} \right] \quad (5)$$

where  $A_{\text{SN}}$  and  $A'_{\text{SN}}$  are uncorrected and corrected net activities of sample.

#### Initial radiocarbon concentration

Sometimes the initial concentration of  $^{14}\text{C}$  atoms in a sample can be different from the  $^{14}\text{C}$  concentration in the atmosphere. For instance, underground aquifers contain carbon dissolved in form of soluble carbonates or bicarbonates which does not originate exclusively from atmospheric carbon dioxide. The amount of dissolved calcium carbonate depends on the dissolved  $\text{CO}_2$  according to the relation:



where  $\text{C}^x$  denotes active biospheric carbon (developing from decomposing organic material in the soil) which has the same activity as plants, and the calcite carbon which contains no  $^{14}\text{C}$  because is several million years old. According to (6) the ratio of organic to anorganic carbon would be 50% : 50%, which means that the initial specific activity of  $^{14}\text{C}$  atoms would be half of the initial activity in contemporary plants (7). It was measured on the contrary that the activity of hydrocarbonates was between 65% and 100% modern instead of 50% as expected according to (8).

This ratio depends on the nature of the soil through which water is seeping on the way to the underground reservoir. For Karstic areas of Yugoslavia this ratio is between 0.65 and 0.85.

For initial activity less than 100% (underground aquifers) argument of the logarithm in relation (7) for age calculation has to be multiplied by this factor. The influence of this correction is linear so that it is the most significant for age measurements of younger waters.

The influence of the initial radiocarbon concentration is presented on an example for 3 water samples of different ages:

Initial $^{14}\text{C}$ activity	100%	85%	65%
Sample	age (years)	age (years)	age (years)
Water Libya S-2	36,800	35,500	33,360
Water Libya S-8	23,650	22,350	20,200
Plitvice "Bijela rijeka"	2224	919	-1235

#### Sample contamination

Besides minor changes in the specific activity of carbon in the biosphere caused by variation of cosmic flux, the climate changes and the carbon reservoir, man activities disrupted completely the equilibrium of  $^{14}\text{C}/^{12}\text{C}$  ratio which has been established over millenia.

There are two main processes leading to the change of  $^{14}\text{C}$  equilibrium:

- combustion of great amounts of fossil fuel, mainly coal and oil;
- nuclear processes (fission and fusion) in the atmosphere producing great amounts of neutrons.

The quantity of  $^{12}\text{C}$  increases by combustion of fossil fuel, contaminating samples with inactive carbon. By measuring radiocarbon activity of trees whose ages were well known Suess (10) showed that the  $^{14}\text{C}$  activity of wood grown in post-industrial era has been reduced by dilution of atmosphere  $\text{CO}_2$  with fossil  $\text{CO}_2$ .

The second effect resulting from nuclear and thermonuclear explosions, especially in the period 1954-1969, exceeds the first one and has the opposite effect. The  $^{14}\text{C}$  activity of atmospheric  $\text{CO}_2$  increased due to nuclear explosions by factor of 2 in the northern hemisphere during the bomb test period.

#### Standard for radiocarbon dating

The oxalic acid supplied by the US National Bureau for Standards (NBS Oxalic acid) has been adopted as an international standard for radiocarbon age measurements. In absence of oxalic acid standard some substandards can be used. The 95% value of oxalic activity in 1950, normalised for  $\delta^{13}\text{C}$  on -19‰ has been adopted as the standard. Although the oxalic acid activity decreases in time, the absolute international standard (AISA) does not change, when properly corrected for decay of  $^{14}\text{C}$  atoms:

$$A'_{\text{AISA}} = A'_{\text{ON}} \cdot e^{\lambda_2(y-1950)} \quad (7)$$

where  $y$  is the year of measuring of the oxalic acid activity and  $\lambda_2$  is the disintegration constant related to  $^{14}\text{C}$  half-life (5730 years). Oxalic acid activity corrected for isotopic fractionation is:

$$A'_{\text{ON}} = A_{\text{ON}} \left[ 1 - \frac{2(19 + \delta^{13}\text{C})}{1000} \right] \quad (8)$$

where  $A_{\text{ON}}$  is net oxalic activity.

### Counting errors

Measurement of sample activity in  $^{14}\text{C}$  laboratory of Rudjer Bošković Institute lasts 24 to 48 hours in 20 min. time intervals in a proportional counter filled with methane which is prepared from sample, by combusting it to  $\text{CO}_2$  and converting  $\text{CO}_2$  to  $\text{CH}_4$ . The age is, according to (3):

$$t = \tau \cdot \ln \frac{A_{\text{ON}}}{A_{\text{SN}}} = \tau \cdot \ln \frac{(A_{\text{O}} - A_{\text{B}}) \cdot 0.95}{A_{\text{S}} - A_{\text{B}}} \quad (9)$$

where  $A_{\text{ON}}$  and  $A_{\text{SN}}$  are the net mean count per minute of standard and of the sample respectively, obtained by subtraction of the background mean count  $A_{\text{B}}$  per minute from  $A_{\text{O}}$  and  $A_{\text{S}}$ , respectively. According to the law of error propagation the standard deviation of the age is:

$$\sigma_t^2 = \left(\frac{\partial t}{\partial \tau}\right)^2 \sigma_\tau^2 + \left(\frac{\partial t}{\partial A_{\text{ON}}}\right)^2 \sigma_{A_{\text{ON}}}^2 + \left(\frac{\partial t}{\partial A_{\text{SN}}}\right)^2 \sigma_{A_{\text{SN}}}^2 \quad (10)$$

Neglecting the error in the half-life, one obtains:

$$\sigma_t^2 = \frac{\tau^2}{t_m} \left[ \frac{A_{\text{ON}} + 2A_{\text{B}}}{A_{\text{ON}}} + \frac{A_{\text{SN}} + 2A_{\text{B}}}{A_{\text{SN}}} \right] \quad (10')$$

Here  $t_m$  is the measurement duration. The maximum age which is possible to measure is given by the relation:

$$t_{\text{max}} = \ln \frac{A_{\text{ON}}}{A_{\text{B}}} \sqrt{\frac{t_m}{8}} \quad (11)$$

For the measurement period of 48 hours the maximum age is 42 000 years. This represents the lowest dating limit in  $^{14}\text{C}$  laboratory of Rudjer Bošković Institute.

In some cases it may happen that the amount of  $\text{CH}_4$  is too small to fill the counter. The counter must be filled up to the necessary pressure with inactive sample correcting then the count per minute as follows:

$$x_i = A_B + (x_i - A_B) \cdot P \quad (12)$$

Here the ratio between the sum of partial pressures of the sample gas and inactive gas and the partial pressure of the sample is  $P = (P_S + P_B)/P_S$ . The standard deviation and the count per minute errors are

$$\sigma = \frac{P}{I} \sqrt{\frac{x_i^+}{n}} \quad s = \frac{1}{I} \sqrt{\frac{\sum (x_i^+ - \bar{x}^+)^2}{n(n-1)}} \quad (13)$$

where  $I$  is the measurement interval (20 minutes) and  $n$  is the number of intervals ( $t_m = I \cdot n$ ).

### Barometric and temperature corrections

The background counting rate changes with the intensity of cosmic rays and depends on the amount of radon and other radioactive isotopes in the atmosphere. This phenomenon is connected to the change of atmospheric pressure. The background counting rate decreases with increasing atmospheric pressure. The background counting rate as well as the counting rates of other measured samples is corrected for changes of barometric pressure during measurements. The correlation between atmospheric pressure and background count has been calculated as follows:

$$k = \frac{\Delta A}{\Delta B} = \frac{A_B(p_0) - A_B(p')}{p_0 - p'} = -0.0135 \text{ imp min}^{-1} \text{ torr}^{-1} \quad (14)$$

where  $p_0$  is the standard atmospheric pressure (mean barometric pressure in Zagreb is 748 mmHg).  $p'$  is the mean atmospheric pressure during

the measurement and  $A_B(p_o)$  and  $A_B(p')$  are respective background counting rates.

To account for temperature changes an additional correction is introduced. This correction is equal to the ratio of temperature in the moment of filling the counter with the sample  $T'$  and the mean temperature  $T_o$  in the laboratory (for Rudjer Bošković Institute  $^{14}\text{C}$  laboratory this value is  $18^\circ\text{C}$ ). The density of the gas in the counter changes with temperature which causes the change of measured activity. The correction for temperature and barometric pressure changes is:

$$A_S(p_o, T_o) = \bar{A}_B(p_o, T_o) + \left\{ A_S(p', T') - \left[ \bar{A}_B(p_o, T_o) - K \cdot \Delta p \right] \right\} \frac{T'}{T_o} \quad (15)$$

the age of samples is:

$$t = \frac{(A_o - \bar{A}_o) \cdot 0.95}{A_S - A_B} = \tau \cdot \ln \frac{A_{ON}}{A_{SN}} \quad (16)$$

where  $\bar{A}_B = \bar{A}_B(p_o, T_o)$  and  $\bar{A}_o = \bar{A}_o(p_o, B_o)$  are counts per minute standardized values for background and oxalic acid standard obtained as the results of consecutive measurements and application of relation (15).

The final expression for age of the sample is obtained by including the isotopic fractionation correction according to the relation (5) and (8) into the Eq. (16):

$$t = \tau \cdot \ln \frac{A'_{ON}}{A'_{SN}} = \tau \cdot \ln \left\{ \frac{A_{ON} \left[ 1 - \frac{2}{1000} (19 + \delta^{13}\text{C}) \right]}{A_{SN} \left[ 1 - \frac{2}{1000} (25 - \delta^{13}\text{C}) \right]} \right\} \quad (17)$$

The calculated age in this way is the conventional radiocarbon age where the mean half-life of  $^{14}\text{C}$  is 8030 years.

Depletion or enrichment wrt. standard

The relative differences between sample activity and the oxalic acid corrected for  $\delta^{13}\text{C}$  are given according to (12) as:

$$\delta^{14}\text{C} = \frac{A_{\text{SN}}' - A_{\text{ON}}'}{A_{\text{ON}}'} \cdot 1000\% = \left( \frac{A_{\text{SN}}'}{A_{\text{ON}}'} - 1 \right) \cdot 1000\% \quad (18)$$

For  $\delta^{13}\text{C}$  corrected samples:

$$D^{14}\text{C} = \frac{A_{\text{SN}}' - A_{\text{ON}}'}{A_{\text{ON}}'} \cdot 1000\% = \left( \frac{A_{\text{SN}}'}{A_{\text{ON}}'} - 1 \right) \cdot 1000\% \quad (19)$$

By combining with the relation (5) one obtains:

$$D^{14}\text{C} = d^{14}\text{C} - 2(\delta^{13}\text{C} + 25) \left( 1 + \frac{d^{14}\text{C}}{1000} \right) \quad (20)$$

The conventional age can be written as:

$$t = \tau \cdot \ln \frac{A_{\text{ON}}'}{A_{\text{SN}}'} = - \ln \frac{A_{\text{SN}}'}{A_{\text{ON}}'} = - \ln \left( 1 + \frac{D^{14}\text{C}}{1000} \right) \quad (21)$$

The activity of the sample and activity of the standard has to be measured at the same time (the same year is enough), because both values decrease according to radioactive decay law so that the year of measurement does not influence the result.

### Percent modern

The 8<sup>th</sup> Radiocarbon Dating Conference (New Zealand, 1972) recommended the absolute percent modern instead of the quantity  $D^{14}C$ . It is defined (13) as:

$$pM = \frac{A'_{SN}}{A'_{AISA}} \cdot 1000\% = \frac{A'_{SN}}{A'_{ON} e^{\lambda_2(y-1950)}} \cdot 100\% \quad (22)$$

and is connected with the conventional radiocarbon age by the relation:

$$t = \frac{y - 1950}{1.03} = \tau_1 \cdot \ln \frac{pM}{100} \quad (23)$$

The conventional radiocarbon age has been calculated with  $\tau_1$ , and AISA has been defined with  $\tau_2$ . Hence the factor 1.03 in Eq. (23).

It is very convenient to express geochemical results as "percent modern" rather than using conventional radiocarbon age. The expression "age" has no meaning for these samples, especially if the samples are contaminated with inactive (Suess effect) or with active carbon. Expressing sample activity contaminated with active carbon by means of "ages" would give unreasonable results such as years in the future.

An example for using percent modern as a convenient notation by which the results are expressed are measurements of water, tufa and plants radiocarbon activity from National Park Plitvička jezera, Croatia, Yugoslavia (14). Percent modern for water samples was 85%, for tufa was about 90% and for plants about 130%. In this case the conventional age would result in an underestimation equal to 1300 years for water samples, 850 years for modern tufa and overestimation equal to 2100 for plants!

A particularly interesting case is that of underwater plant (Cratoneurum commutatum) for which we obtained the result  $pM = 91.7 \pm 1.0\%$  that corresponds to 670 years old sample although this plant grew in the 1978! The reason for such results is the mixing of active  $CO_2$  with inactive  $CO_2$  from calcium carbonate. The purpose of investigations of underwater plant radiocarbon activity was to establish the ratio between activity of underwater plants and the surrounding biosphere.

### Age correction

If we want to compare the radiocarbon activity of a sample with the activity of modern standard (oxalic acid) the activity of the sample has to be corrected to the value which would have it the year when the modern standard has been collected. As agreed, both the activity of the sample and the activity of the modern standard must be reduced to the same year (1950). This correction is based on the half-life to which corresponds mean life  $\tau_2$ . A new quantity  $\delta^{14}C$  is defined as a relative difference between the activity of AISA and the activity of the sample corrected for age:

$$\delta^{14}C = \left[ \frac{A_{SN} e^{2(y-x)}}{A_{AISA}} - 1 \right] \cdot 1000\% \quad (24)$$

Here  $y$  is the year of measurement and  $x$  is the year of the sample age which one has to know at such measurements. After normalizing  $\delta^{13}C$  the relative difference between age corrected sample activity and absolute international standard is:

$$\Delta^{14}\text{C} = \left[ \frac{A'_{\text{SN}} e^{\lambda_2(y-x)}}{A_{\text{AISA}}} - 1 \right] 1000\% = \left[ \frac{A'_{\text{SN}} e^{\lambda_2(1950-x)}}{A_{\text{AISA}}} - 1 \right] 1000\% \quad (25)$$

By combining this relation and the expression for  $\delta^{13}\text{C}$  one can obtain an approximative relation:

$$\Delta^{14}\text{C} = \delta^{14}\text{C} - 2(\delta^{13}\text{C} + 25)\left(1 + \frac{\delta^{14}\text{C}}{1000}\right) \cdot 1000\% \quad (26)$$

#### Computer processing of radiocarbon data at Rudjer Bošković Institute

The activity of  $^{14}\text{C}$  is measured in a proportional counter containing 3.3 liters of methane. The measurement is divided into 20 minute time interval to make possible statistical analysis of data and rejection of statistically improbable data resulting from power failures, noise pick up and breakdowns.

Data necessary to process a sample are (15);

- laboratory number and the sample name;
- date of sample combustion and reduction of  $\text{CO}_2$  to  $\text{CH}_4$  together with the obtained amount of gases;
- date of sample measurement;
- mean count per minute of modern standard (oxalic acid) and background;
- $^{13}\text{C}/^{12}\text{C}$  ratio in per mill in relation to PDB standard;
- ratio P, Eq. 12 to fill the counter up to the necessary pressure if there was not enough gas from the sample itself;
- mean atmospheric pressure, temperature and relative humidity in the moment when the counter was filled;
- test of the gas purity obtained by measuring the counting rate due to the  $^{226}\text{Ra}$  source in a fixed position close to the counter in the steep part of the plateau of the proportional counter;

- pulses in anticoincidence measured in twenty-minute intervals.

Top of the computer output list (see the enclosed print-out) contains relevant input data to enable one a quick check up.

All obviously bad count intervals have been rejected by help of the Chauvenet criterion. Counts per interval exceeding certain limit  $z_0$  have been rejected. Here  $z_0$  is defined so that the area under the Gauss curve from  $z_0$  to  $\infty$  must be:

$$P(z_0 \leq z_i < \infty) = \frac{1}{2n} \quad (27)$$

and  $z_i$  are:

$$z_i = \frac{x_i - \bar{x}}{\sqrt{\frac{\sum_{i=1}^n (x_i - \bar{x})^2}{n}}} \quad (28)$$

Input data satisfying the Chauvenet criterion have been divided into groups, each group containing ten inputs. Dissipation from the mean value in percents has been calculated for each group and this is presented by asterisks on the computer output list. A regression and correlation coefficient for anticoincident counting rate intervals has been given too. The total number of counts as well as the mean counting rate is given. According to relation (12) the data are corrected for partial pressure of the active sample.

Test of the sample variance has been given by the limiting value  $g_0$  of the following expression:

$$g = \frac{\sum_{x=1}^n (x_i - \bar{x})^2}{\bar{x}} \quad (29)$$

which for number of pulses  $n = 30$  can be expressed as :

$$g_o = 1/2 (u - \sqrt{2k-1})^2 \quad (30)$$

For 5% significancy  $u = 1.645$  and  $k = n-1$  is number of degrees of freedom.

Counting rates have been corrected for pressure and temperature changes (s.t.p. correction) and have been graphically presented together with their standard deviations as counts per twenty-minute interval, counts per minute (CPM) and counts per minute corrected for standard pressure and temperature.

The results of age measurement have been presented in the following way:

- sample age and the associated error based on Libby half-life;
- sample age corrected for  $^{13}\text{C}$ ;
- sample age calculated on the basis of half-life equal to 5730 yrs, which is simply the previous result multiplied by 1.03;
- dendrochronological correction of the age if an organic sample has been measured.

The initial activity of water, speleothems or tufa is less than the initial activity of the biosphere. An initial activity equal to 85% of modern standard results in the age which is 1305 yrs younger than a standard age.

Dendrochronological correction has been made on the basis of parallel measurements of wood age by radiocarbon method and by dendrochronological method from 5100 B.C. to the middle of the nineteenth century (16).

Results of these measurements are stored in computer memory and are automatically called after the  $^{14}\text{C}$  age for a sample has been calculated in order to print the correction on the list. A polynom has been calculated on the basis of dendrochronological correction by help of least squares method:

$$t_{\text{dendro}} = \left[ Q + (p_1 + Q^2)^{1/2} \right]^{1/3} - \left[ Q - (p_1 + Q^2)^{1/2} \right]^{1/3} - p_2 \quad (31)$$

Where:

$$Q = q_1 + q_2 \cdot t_{^{14}\text{C}}$$

$$p_1 = 1.035 \cdot 10^{22}$$

$$q_1 = 7.24 \cdot 10^{10}$$

$$p_2 = 2.020 \cdot 10^3$$

$$q_2 = 4.24 \cdot 10^7$$

In addition to conventional radiocarbon age expressed in years (using B.C. or A.D. notation) every result has been expressed as  $d^{14}\text{C}$ , percent modern and  $D^{14}\text{C}$ . The last one only if  $\delta^{13}\text{C}$  corrected was made.

The test of last digits of input data is added too. It was of particular interest during the time when a mechanical printer was in use and sometimes happend that one of digit appeared more frequently than the other. The expected value for appearance of the last digit (from 0 to 9) is  $\bar{f} = n/10$  and  $f_i$  is every last digit really printed out. If chisquare test

$$\chi^2 = \sum_{i=1}^I \frac{(f_i - \bar{f})^2}{\bar{f}}$$

gives a value greater than the limit for 10 degrees of freedom (16.919) this test is positive, otherwise is negative.

### Conclusion

The method of radiocarbon dating is in fact a reliable method because it is based on the disintegration of atomic nucleus which is independent from outer physical and chemical factors. The corrections described have not decisive influence on results of measurement but can influence the precision of measurements. Results obtained all over the world as well as in our laboratory are of great use for various scientific disciplines as archaeology, paleontology, geology, hydrology etc. The radiocarbon method of dating has no possibility to tell us the exact year when a building was built, an organism died or some water entered an underground aquifer because every result has an error, but combined sometimes with the results of some other scientific disciplines this method gives very decisive results.

Among many samples which have been measured at Rudjer Bošković Institute for last 10 years were the following: a beam from St. Donat church in Zadar (result:  $702 \pm 23$  A.D.) (17), coal from old Roman town Stobi in Macedonia (1880 to 1620 years old)(18), underground water from Tripolitania region in Libya (19), tufa, underwater plants and water from Plitvice National Park and several hundred hydrological and geochemical samples from Yugoslavia and abroad. Results of these measurements are regularly published in Radiocarbon Journal and are of great interest to many scientists as well as economists.

2-726 PRILJKA 1. HADJAJARIC / 1 . MEASUREMENT: 13.APR 1980 C02: 1.APR 1980 760, MM  
 START: 12.15 END: 8.15 + CH4: 1.APR 1980 980, MM

MEASUREMENT OXALIC ACID BACKGROUND REFERENCE FILLING REFERENCE MEAN BAR. COUNTER PRESSURE REL. HUM. \*\*\*  
 DURATION CPH 27.031- 145 5.084- 0.267 18.0 CELS. 20.0 CELS. 745.0 MM 737.0 MM 2.06 ATP 1.000 (1/4) \*\*\*  
 RATIO: CPH - BEFORE: 1554 1472 1420 1526 1495 1457 MEAN=1472.0 RA TEST: - - - - - +  
 AFTER: 1409 1449 1446 1457 1475 1434 MEAN=1445.0

COUNTS IN ANTICOINCIDENCE ( 611): 517 534 510 497 492

416	475	471	493	442	423	449	461	411	435	4446.0	1.79
473	410	420	397	438	442	437	447	450	4361.0	-0.15	
417	442	429	433	420	420	459	446	419	434	-1.34	
417	446	447	436	421	438	437	411	419	421	4293.0	-1.71
457	435	435	437	466	426	419	431	445	421	4365.0	-1.06
439	421	480	426	441	456	442	435	441	451	4424.0	1.47
414									451.0		

-----  
 26697.0 MEAN: 436.18 INTERCEPT SLOPE CVREL.CUEF  
 438.003 -0.211-000 -0.836-001 +  
 COUNTS PER INTERVAL: 436.180 +- 2.674 SAMPLE DEV.: +- 2.335 CHI SQUARE: 45.74 +  
 COUNTS PER MINUTE: 21.809 +- 0.134 SAMPLE DEV.: +- 0.117 PISS:0.951: 78.80 +  
 CPH (S.T.P. CORR.): 21.769 +- 0.136

AGE(1/2 LIFE 5570) : 2163.7 +- 99.9 YEARS YEAR D.C. 213.7  
 AGE(S.T.P. CORRECTION) : 2183.9 +- 95.0 YEARS YEAR D.C. 233.9 D.C.14: -238.1 +-6.5  
 AGE(1/2 LIFE 5730) : 2289.4 +- 97.8 YEARS YEAR D.C. 277.4 S. MODERN: 75.4 +-0.6  
 AGE(THERMOCORR.) : 2283.0 +- 107.0 YEARS YEAR D.C. 270.0 MASCA CURVE: -274.9 YEARS

COUNTS BELOW 398.41 : ---  
 COUNTS ABOVE 477.95 : 480  
 A.C. COUNTS OUT OF 2-SIGMA : BELOW .00 ABOVE= 1.64 TOTAL= 1.64 \*

COUNTS BELOW 373.53 : ---  
 COUNTS ABOVE 499.64 : ---  
 A.C. COUNTS OUT OF 3-SIGMA : BELOW .00 ABOVE= .00 TOTAL= .00 \*

LAST DIGITS 5: 1=21,31 2= 6,56 3= 6,56 4= 1,64 5= 9,04 6=13,11 7=13,11 8= 4,92 9=13,11 0= 9,84 CHI SQUARE: 16.07  
 P(9,0.05) : 16.92  
 COMMENT :

Table: Computer output list with 14 C results and statistical tests.

### Acknowledgement

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