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A 23-YEAR RETROSPECTIVE BLIND CHECK OF ACCURACY OF THE COPENHAGEN RADIOCARBON DATING SYSTEM

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ABSTRACT. A 23-yr record of the measuring accuracy of the Copenhagen radiocarbon dating laboratory has retrospectively been provided through a true blind test. A total of 92 samples of oak from old tree trunks were dated in the period 1971 to 1993 and their dendrochronological age determined independently. The ^{14}C activity of the dendrochronological samples measured in the Copenhagen radiocarbon laboratory was compared to the activity of the tree rings of the same age measured by Stuiver and Pearson (1993) for calibration purposes. The average difference was found to be 54 ± 72 ^{14}C yr. The results further indicate that the actual standard deviation is only 7% higher than that quoted by the laboratory. The investigation has shown a long-term stability of laboratory accuracy with no systematic laboratory variations either with respect to sample age or to the time of measurement from 1971 to 1993.

INTRODUCTION

Quality assurance is vital for a sustained confidence in radiocarbon dates. This was clearly displayed by the results of the International Collective Study conducted by ^{14}C-dating laboratories, which demonstrated the importance of a constant attention to factors influencing the general accuracy of ^{14}C measurements and to the danger of laboratory bias (Long 1990; Scott et al. 1998). Quality control is the responsibility of the individual ^{14}C laboratory, which should engage in a formal quality program in order to dispel the doubts and distrust that are sometimes voiced against the method, for example by Pilcher (1993), who somewhat belligerently concluded that ^{14}C dates should rather be considered as "reasonable estimates of the nearest half millennium in which the sample falls". The present investigation shows that ordinary laboratory ^{14}C dating, if properly performed and controlled, can be much better than that.

One means of quality control in the ^{14}C laboratory is measuring samples that can later be dated by independent methods. This was realized already by Tauber (1977), when the first 12 samples of oak (*Quercus* sp.) were dated in the Copenhagen ^{14}C laboratory. Altogether, 92 such samples have been dated here in order to facilitate the building of a Danish dendrochronological master chronology. When found, oak samples judged suitable for contributing to the master chronology were sent to the laboratory in order to provide an approximate age for the dendrochronologists. Once the specimen was dendrochronologically dated and the dendrochronological series had been firmly connected to the present, an absolute age could be assigned to the ^{14}C-dated sample. The absolute age was thus unknown to the ^{14}C laboratory at the time of dating, and the final dendrochronological age provided a check on the overall precision of the laboratory.

The standard deviation of a ^{14}C age is estimated from the counting statistics of the sample, the background, and the modern sample; together, these are called the combined counting statistics. This figure does not, however, include all types of variability introduced in the various steps of the dating process, according to the proposed quality assurance protocol for ^{14}C-dating laboratories (Long 1990).

A comparison between the abovementioned ^{14}C ages and the corresponding dendrochronological ages provides a good measure of the total analytical precision of a ^{14}C dating laboratory, and the

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fairly regularly performed datings of such samples thus give a reasonable estimate of the total analytical precision of the Copenhagen radiocarbon laboratory for the last 23 yr. No oak sample that has been dated by both the ^{14}C method and by dendrochronology in Copenhagen has been left out of the present study.

THE ^{14}C METHOD

The Copenhagen ^{14}C laboratory utilizes a 2.0 L conventional gas-proportional counter now equipped with a gas-proportional guard counter. Until 1991, however, the guard system consisted of 17 Geiger counters in an overlapping half-circle geometry. The change from 180° Geiger counters to a 360° proportional counter took place in January 1991. Prior to moving the laboratory in 1989, the background count rate in the Copenhagen ^{14}C laboratory was ca. 3.1 cpm; after the counting equipment was moved to a new location in a smaller and less massive building, the background count rate with the Geiger counters went up to ca. 3.7 cpm. Installing the 360° gas proportional guard counter resulted in a background count rate of ca. 3.1 cpm. Thus the background count rate is presently, and has for the bulk of the time been, ca. 3.1 cpm.

The activity of 0.95 times that of HOxI, corrected for background has been approximately 17 cpm in this system.

Wood samples are normally subjected to the standard A-A-A treatment prior to analysis in our laboratory. Slight modifications to the procedure are used for more decomposed samples, very few of which are in the present data set. The samples are burned to CO_2 in 6 atmospheres of pure oxygen in a Phonon bomb (manufactured by BJ Precision Engineering Co., Norfolk, England). The water is separated, and the sample is dissolved in NH_4OH and later precipitated with $CaCl_2$ and washed on a filter with hot water to remove soluble carbonates and excess of hydroxide. The carbonate is kept precipitated in water in sealed flasks for at least 3 weeks in order to let the bulk of possible ^{222}Rn decay (ca. 6 half-lives). The samples are then converted to CO_2 again and admitted to our preparation line. Here they are purified in an oven with CaO prepared from pure Icelandic double spar. Memory effects are avoided by baking the CaO-oven for several hours at elevated temperatures between each purification. After purification, the sample is transferred to the counter.

A total of about 1.5 g of carbon is counted. The counting pressures of samples, blanks, and oxalic acids are always kept between 1098 and 1102 mm Hg, and monitored and corrected to within an accuracy of ±0.1 mm Hg. Before and after the counting of each sample, a sealed ^{60}Co source with a known activity is introduced at a fixed position near the counter and the count rate measured for 5 min at an interval of 50 V. This gives both the plateau and the proper working voltage. A precalculated count rate from the ^{60}Co source is selected 500 V below the plateau, where the count rate versus high tension curve is most sensitive. The working voltage is then set to this value plus 500 V and adjusted to within ±5 V. Any contamination of the sample from electronegative gases (e.g., H_2O, O_2, SO_2 or NO) is detected here and if a sample is contaminated, it is taken back in the preparation line for further purification. The samples are counted for at least 20 h in the 2.0 L 1100 mm Hg conventional proportional counter. The air pressure, temperature and humidity are measured throughout the operation, and small corrections due to variations in these values are applied to the date. After amplification, discrimination and pulse-shaping, the pulses from both the central counter and the guard counter are registered on a data acquisition board in a computer. The total number of anticoincidence, coincidence and total guard counter counts is stored each hour. At the end of the measurement these totals are plotted, and visual inspection performed to verify that no systematic errors have occurred, in other words, that the variations in counting rate are in agreement with the expected

statistical bounds. Prior to the installation of data collection hardware, control was ensured by taking frequent readings during working hours.

Blanks are prepared from large single crystals of Icelandic double spar, which are etched in HCl to 80% of their initial weight in order to remove any surface contamination. Blanks are measured for 1 day every second week, and so are the NIST oxalic acid samples (HOxI, 1950). Our HOxI samples are prepared in strict accordance with the recommendations in Valastro et al. (1977), and $\delta^{13}C$ values of the oxalic acid samples over the 3 years 1992–1993 average to $-19.9 \pm 0.5‰$ VPDB, which is very close to what is expected (−19.1‰) according to Valastro et al. (1977). We still use oxalic acid from the original NBS 5-pound jar.

Stable isotope values ($\delta^{13}C$) have been measured on all samples dated from 1975 onwards. The accuracy of the mass spectroscopic measurements is now better than ±0.03‰ VPDB, and has in the past probably been better than 0.1‰ VPDB. Dates are corrected to $\delta^{13}C = -25‰$ VPDB. Dates produced prior to 1975, when stable isotope fractionation was not measured, are assigned an extra uncertainty, and the uncertainties on these samples were never quoted as less than ±100 yr. The average $\delta^{13}C$ of the oak samples turns out to be $-24.9 \pm 1.0‰$ VPDB, which is also in full agreement with what is expected from rather well-preserved wood samples. Once in the preparation line the dendrochronological samples, the oxalic acid samples and the blank samples are treated identically. The same 2 laboratory assistants prepared all samples included in the present study.

Calibration of conventional ages is performed with the University of Washington program CALIB version 3.0.3C using the 20-yr averaged atmospheric curve, and we have used intervals of calibrated ages at $\pm 1\sigma$ calculated by method A (Stuiver and Reimer 1993; Stuiver and Pearson 1993; Pearson and Stuiver 1993).

THE DENDROCHRONOLOGICAL METHOD

The dendrochronological dates are based on the assumption that trees that grew under the same environmental conditions over the same period of time contain similar tree-ring width patterns.

A master chronology for oak (*Quercus* sp.) has been established in Denmark for dating purposes back to around 100 BC (Bonde et al. 1994). For the older periods 2 Danish chronologies relevant to the present study were dated absolutely by comparison with German master chronologies, the Danish chronologies covering the periods 2955–2483 BC and 2069–401 BC (Christensen 1997). All samples are measured with a binocular microscope at magnifications of 10–40×. The tree-ring series are measured twice, preferably on different radii. The measured tree-ring width patterns are plotted for visual inspection and an average of the 2 curves is used for dating. The tree-ring patterns are compared to the established tree-ring chronology using various standard computer programs such as CROSS (Baillie and Pilcher 1973), CATRAS (Aniol 1983), and DENDRO (Tyers 1997). The samples submitted for ^{14}C dating usually consisted of 20–30 tree rings.

The reported dendrochronological dates in this paper are the dates of the middle tree ring submitted for ^{14}C dating. The curvature of the tree rings in the wood samples will lead to a slight overweighting of material from juvenile rings. With the typical sizes of oak trees in question and typical distances from the center of the tree, this error will normally be < 1 yr.

RESULTS AND DISCUSSION

Because of irregular wiggles in the calibration curves, there is no simple, unique way of comparing the calibrated ^{14}C dates with the corresponding dendrochronological midpoint dates.

One way to get an approximate measure of the difference between the 2 data sets is to compare the dendrochronological midpoint ages with ages of the midpoints of the ± 1σ intervals of the calibrated ^{14}C dates. Calculated this way, the average difference between the 2 data sets is 52 ± 85 calendar years, the ^{14}C ages being younger than the dendrochronological ages. The mean difference of 52 yr is well within the ± 1σ interval. As the ± 1σ intervals for the calibrated ^{14}C dates are often asymmetrically distributed, differences calculated in this way may tend to be slightly exaggerated. Even so, 55% of the 92 dendrochronological midpoint ages lie within the ± 1σ interval of the calibrated ^{14}C age, and 90% within the ± 2σ interval, which is close to the expected values.

Another, more direct, way of establishing the difference between the 2 data sets is to compare uncalibrated ^{14}C ages. With a known dendrochronological age for each sample, the conventional ^{14}C age determined in the Copenhagen laboratory can be directly compared to the conventional ^{14}C age of the dendrochronological sample of the same age measured by Stuiver and Pearson (1993) in the construction of the bidecadal calibration curve. In Figure 1 the conventional ages measured in the Copenhagen laboratory are shown as a function of the corresponding conventional ages measured by Stuiver and Pearson (1993). The line of identical ages is also shown. The agreement is good throughout the entire age span covered by the investigation.

We have calculated the differences by subtracting the Danish dates from the selected calibration curve dates, and calculated the standard deviation of each difference as the square root of the sum of

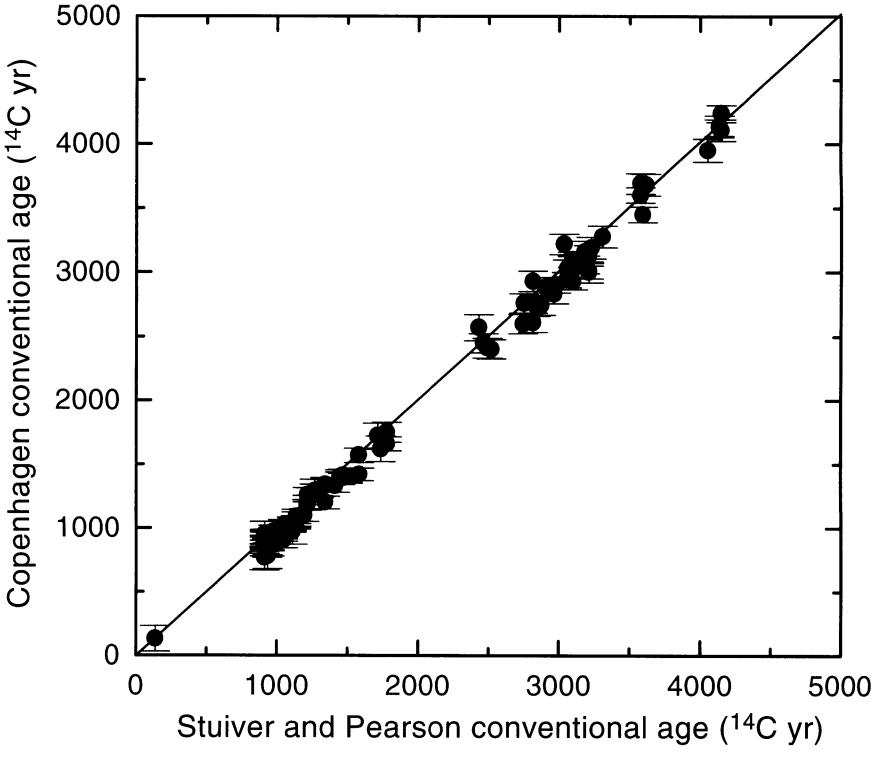

Figure 1 Conventional ^{14}C ages measured in the Copenhagen radiocarbon laboratory as a function of conventional ^{14}C ages of dendrochronologically dated samples of the same age selected from the Stuiver and Pearson (1993) bidecadal calibration curve. The straight line shows identical ages.

squares of the 2 standard deviations. The average standard deviation is ± 12 ^{14}C yr for the calibration curve dates, and ± 67 ^{14}C yr for the Copenhagen dates. The average difference between the 2 data sets is 54 ± 72 ^{14}C yr, the Copenhagen dates being younger than the calibration curve dates. Again the average difference of 54 ^{14}C yr is well within the ± 1σ interval. The distribution of the differences is shown in Figure 2.

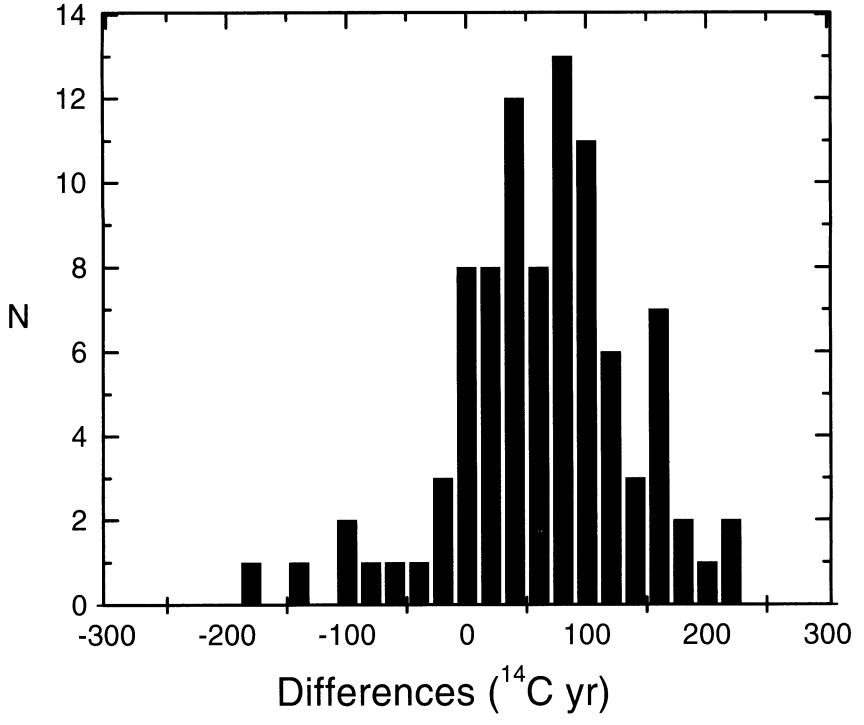

Figure 2 The distribution of the differences between conventional ^{14}C ages of dendrochronologically dated samples selected from the bidecadal calibration curve of Stuiver and Pearson (1993) and conventional ^{14}C ages of samples of the same dendrochronological age measured by the Copenhagen laboratory.

The average standard deviation of the uncalibrated ^{14}C dates measured in Copenhagen of ± 67 ^{14}C yr is very close to the value of ± 72 ^{14}C yr found from the differences. The ratio K of the actual mean standard deviation (72 ^{14}C yr) divided by the quoted mean standard deviation (67 ^{14}C yr) is a convenient measure of the degree to which the quoted standard deviation is representative of the overall uncertainty in a ^{14}C date. From the present study, the K-value of the 92 ^{14}C dates made by the Copenhagen laboratory is found to be 1.07, which means that the quoted standard deviations have, on average, been only 7% too low throughout the period covered by the investigation.

In 1990, an intensified scheme of measuring blanks and oxalic acids was introduced in the laboratory procedure. At about the same time a proportional gas guard counter and computerized data collection were installed. Although based on only 11 samples, the measured differences relative to Stuiver and Pearson (1993) for the following period were only 10 ± 95 ^{14}C yr, which suggests that the possible bias has been considerably reduced or has disappeared following these improvements. As a quality assurance program we will further monitor our system in the future, utilizing dendro-

chronologically dated samples and other samples of known ages, and hope in this way to continue improving its precision.

An important question is whether the differences between uncalibrated ^{14}C ages of corresponding samples measured in the Copenhagen laboratory and by Stuiver and Pearson (1993) show systematic variations with respect to the time at which the ^{14}C dating was performed in the Copenhagen laboratory. In Figure 3 the differences are shown as a function of the time of measurement in the Copenhagen laboratory. Although the dating activity of dendrochronological samples has not been constant throughout the period of analysis, Figure 3 shows no systematic increase or decrease during the 23 yr covered by this investigation. One might speculate whether there are small jumps at around days 1800 and 7000. If the time series is divided up into 3 subseries, from 0–1776, 1813–6807 and 7071–8188, the average differences become 49 ± 76, 62 ± 62 and 9 ± 95 ^{14}C yr. If, however, the lowest point in the first subseries is removed, the average difference here becomes 61 ± 62 ^{14}C yr, or exactly the same as in the second subseries. So we can conclude that there is no significant jump at day 1800. Even if it is not statistically significant, the jump at day 7000 seems more substantial, and as noted above it is probably due to the introduction of the gas guard counter system and the intensified scheme of measuring standards.

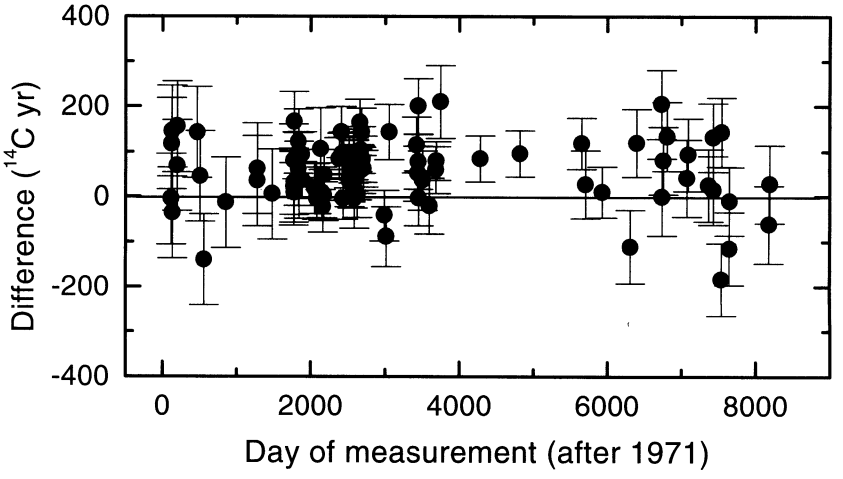

Figure 3 The differences between conventional ^{14}C ages selected from the bidecadal calibration curve of Stuiver and Pearson (1993) and conventional ^{14}C ages of samples of the same dendrochronological age measured in Copenhagen, shown as a function of time of measurement in the Copenhagen laboratory. Combined uncertainties are shown as ±1σ. No systematic variations are discernible with respect to measuring time.

CONCLUSION

Ninety-two oak samples dated in the Copenhagen ^{14}C laboratory have subsequently been dendrochronologically dated. The average difference between the dendrochronological midpoint dates and the mean ages of the ± 1σ intervals of the calibrated ^{14}C dates was 52 ± 85 calendar years. The average difference between the conventional ages measured in Copenhagen and the conventional ages of the dendrochronologically dated samples of the same age measured by Stuiver and Pearson (1993) for their calibration curve was found to be 54 ± 72 ^{14}C yr. Both comparisons show a good agreement, well within ± 1σ, between ^{14}C measurements made in Copenhagen and the Stuiver and Pearson (1993) calibration curve measurements. The standard deviation of 72 yr is very close to the aver-

age standard deviation of the conventional ^{14}C dates of 67 yr, the ratio K being 1.07. No systematic laboratory variations in the ^{14}C dates have been detected, either as a function of sample age or as a function of time of measurement from 1971 to 1993.

It should be stressed that the 92 oak samples dated in the Copenhagen ^{14}C laboratory were not sampled for the purpose of monitoring the accuracy of the laboratory, but were received by the laboratory over the last 23 yr for the specific purpose of establishing a master chronology for oak for the Danish area. So these randomly selected samples are in all respects ordinary samples from different periods treated according to the normal procedures in the laboratory. This demonstrates that good accuracy can be obtained in ^{14}C dating if constant and thorough effort is practiced in the ^{14}C laboratory.

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