RADIOCARBON, Vol 53, Nr 3, 2011, p 543–550

APPLICATION OF THE TRIPLE-PHOTOMULTIPLIER LIQUID SPECTROMETER HIDEX 300 SL IN RADIOCARBON DATING

Marek Krąpiec

AGH University of Science and Technology, Faculty of Geology, Geophysics and Environmental Protection, Al. Mickiewicza 30, 30-059 Kraków, Poland. Also: Laboratory of Absolute Dating, Cianowice 225, 32-043 Skała, Poland.

Adam Walanus

AGH University of Science and Technology, Faculty of Geology, Geophysics and Environmental Protection, Al. Mickiewicza 30, 30-059 Kraków, Poland. Corresponding author. Email: walanus@geol.agh.edu.pl.

ABSTRACT. The Hidex 300 SL is a liquid scintillation analyzer with an automatic sample changer and a triple-photomultiplier tube detection assembly that registers triple- as well as double-coincidence spectra. In the triple mode, the background in the ^{14}C window is 13.7 cpm (^{14}C standard 30.8 cpm; =154.3 cpm/5.01), so the factor of merit equals 8.7. The triple-to-double coincidence ratio (TDCR) allows for determining the ^{14}C counting efficiency, the quench level, and quench correction. However, in the case of very low-activity samples, which is the case even for modern ^{14}C samples, the TDCR is not the best method for the correction of benzene impurities. We propose using the position (channel) of the right slope of the sample (^{14}C) logarithmic pulse-height spectrum. In the case of near-background samples, the cosmic muon peak can be used instead. The Monte Carlo modeling of spectra gave the ^{14}C level below which the muon peak is a better quench correction parameter than the position of the ^{14}C spectrum. The spectrometer, with the proposed quench correction method, was tested with wood samples dated dendrochronologically. For 21 samples, there is no systematic bias observed, and the standard deviation of the age differences scaled by the Poisson errors is 1.24 ± 0.15, which means that the counting statistics account for 80% of the total variability (including sample preparation).

THE SPECTROMETER

A Hidex 300 SL is in operation in the Laboratory of Absolute Dating, Skała, Poland, for dendrochronological studies (Krąpiec 1992, 2001). Radiocarbon dating is necessary here for determining the position of floating chronologies, as well as for wiggle-match dating of individual tree-ring sequences. The coincidence of 2 independent methods makes this the ideal place for testing a new device.

The Hidex 300 SL has a compact design and weighs only 128 kg. According to the manufacturer, it is an "automated TDCR scintillation counter" (automation comes with a container that holds 96 vials of 7 mL size or 40 × 20 mL). The triple-to-double coincidence ratio (TDCR) (Simpson and Meyer 1994; Broda 2003) is available due to the counter's 3 photomultiplier tubes, which are arranged symmetrically (120°). The background level of the device is not optimal. In our instrument, there is no external gamma source for sample purity estimation.

Figure 1 presents the spectra of the benzene samples for the 501-pMC ^{14}C standard, a near-modern sample, as well as a blank sample. The "^{14}C window" is chosen to maximize the factor of merit (McCormac 1992), although the elimination of ^{3}H scintillation is also taken into account.

TRIPLE AND DOUBLE COINCIDENCES IN THE ^{14}C WINDOW

TDCR is a liquid scintillation method for determining the absolute activity of beta emitters. TDCR has a value from 1.0 to 0, with 1.0 for 100% detection efficiency. The triple coincidences result in a lower background, compared to the double coincidences. This is evident especially for low energies (Figure 2). The double- and triple-coincidence backgrounds (in the ^{14}C window) are 20.0 and 13.7 cpm, respectively (with 5 g of benzene). However, the activity standard is only smaller by 0.3% for the triple versus the double coincidences. The very low loss of ^{14}C counts, in the case of the triple coincidences, is related to the observed irrelevance of the TDCR correction method.

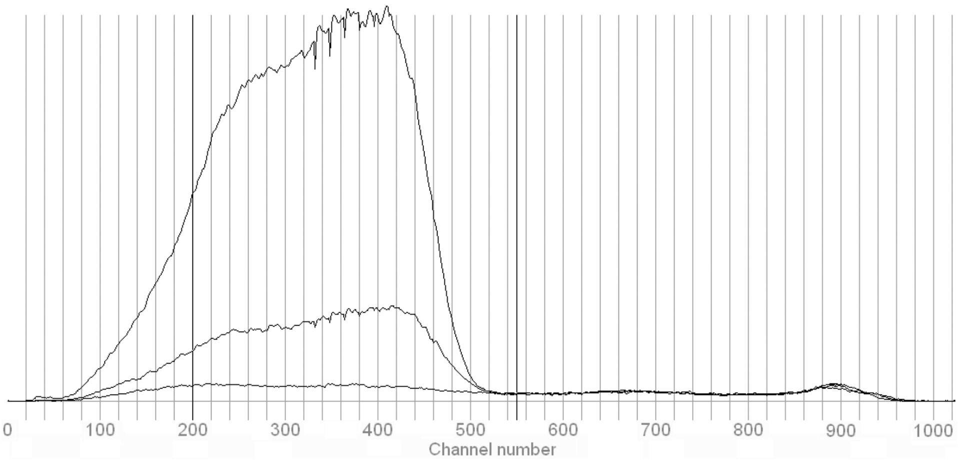

Figure 1 Triple-coincidence spectra (1024 channels) of the ^{14}C activity standard (501 pMC), the 98.3-pMC (140 BP) sample, and background. Measurement time is ~20 hr for each spectrum. The ^{14}C window is indicated. The small muon peak, independent of the ^{14}C content, is visible at about channel 900. The figure has been generated in our dedicated data processing software.

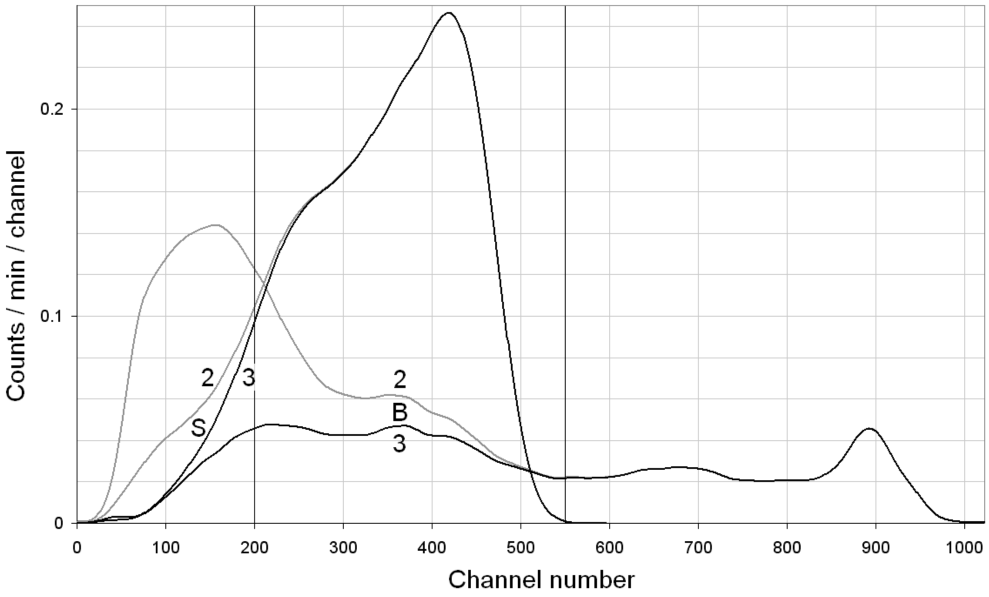

Figure 2 Triple (3) and double (2) coincidence spectra of the ^{14}C activity standard (S) and background (B). The standard is reduced by a factor of 5.01 because its activity is 501 pMC. The S is given with B subtracted. Gaussian smoothing of the curves (σ = 10 channels) has been applied.

TDCR QUENCH CORRECTION

The ^{14}C counting efficiency can be derived from the value of the TDCR parameter and is, therefore, in principle, suitable for quench correction. To examine the TDCR, we produced 6 samples of standard 501 pMC activity with 1 to 6 drops of chloroform added for quenching. The counting rate for these samples (plus the pure one) versus the TDCR parameter is almost perfectly linear (Figure 3).

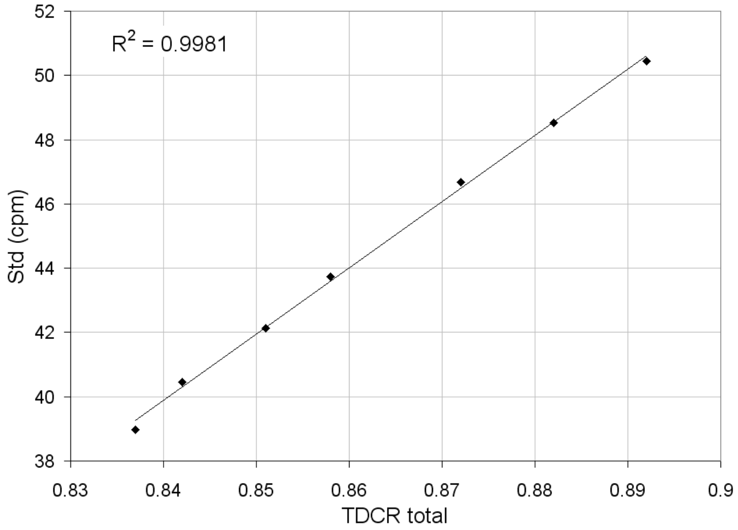

Figure 3 Dependence of the activity standard counting rate on the TDCR parameter for artificially quenched samples. TDCR is calculated for total counts, in all channels (with no any background subtraction), while the sample counts are from the ^{14}C window. If the TDCR is also calculated only in the ^{14}C window, the relationship is slightly more noisy: $R^2=0.9806$ instead of 0.9981.

QUENCH CORRECTION BY ^{14}C SPECTRUM SHIFT

A problem rises, however, with less-active samples due to the shape of the background spectrum. The relationship of the number of quenched sample counts to the TDCR became much weaker as samples moved closer to the background. While there is in general a correct relationship of counts to TDCR (positive correlation), the rise of both background counts and TDCR with the benzene impurity level is contrary to the common idea of the TDCR method (Figure 4). It is therefore clear that the TDCR method is inadequate for old and probably also moderately old ^{14}C samples. This was the reason for developing another method of quench correction (however, with no additional mechanically operated devices, like an external radioactive source).

As discussed below, the method proposed operates better than TDCR even for modern samples. The pulse-height spectra of artificially quenched standards, with a nice, relatively sharp right edge at the upper end, are presented in Figure 5. A quantification of the “right-slope position” is necessary.

As a fit to the right slope of the ^{14}C spectrum, the simple sigmoid function:

$$y = 1-1/(1+\exp(-x))$$

appears to be adequate. However, the formula needs a parameterization. Namely, the sigmoid is to be linearly transformed along the x as well as y axis:

$$y = b+a \times (1-1/(1+\exp(-(x-\text{ChB})/s)))$$

where x is a channel number and y is the counting rate per channel. The parameters are the following: ChB, the critical parameter responsible for the left-right sigmoid movement, in order to quantify the quenching effect (Ch is for channel, B for beta peak) instead of the muon one, to be considered later; s, the sigmoid slope, is to be fitted for better ChB estimation; b, the starting point in terms

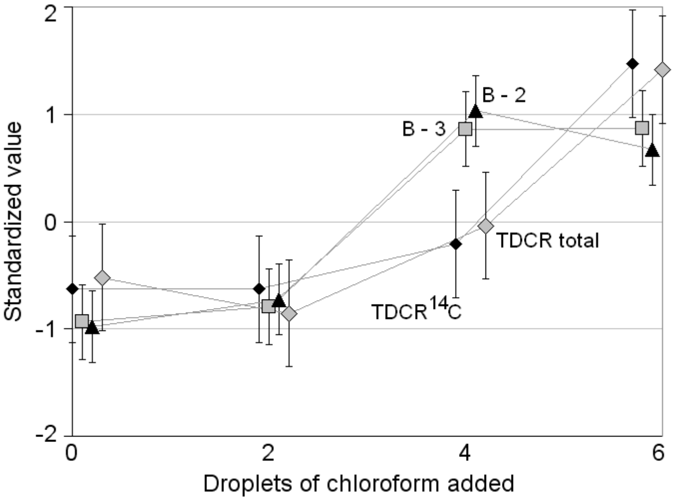

Figure 4 Dependence of background and TDCR on benzene purity. The background is for triple and double coincidences; TDCR for total channels, as well as for the ^{14}C window only. To obtain comparable vertical scales, the 4 variables are standardized by average subtraction and standard deviation division.

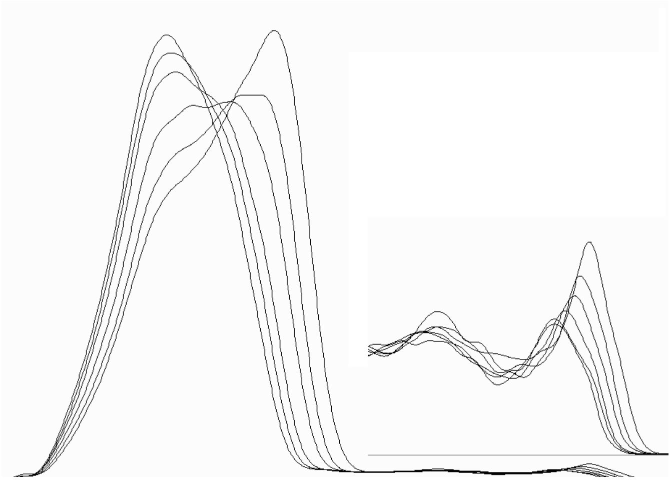

Figure 5 ^{14}C spectra obtained with benzene quenched with chloroform. The right-most curve is not quenched, while the others have approximately the same amount of chloroform sequentially added. The zoomed high-energy part of the spectrum is due to cosmic muons. Curves are smoothed.

of the counting rate, taken as the average value for higher channels; and *a*, the maximal counting rate, dependent on the actual sample activity.

The 4 parameters are estimated for the given measured spectrum (with no background subtraction). The algorithm of estimation is optimized to the problem, with the computer code simplicity taken also as an factor. First, the less essential parameters (*a* and *b*) relevant to the vertical axis are calculated. Initially, the value a_1 is computed as follows. The channel of maximal counts is detected, and the average value for the surrounding ±10 channels is then calculated, as a_1. The b is calculated in a similar way but the lowest channel is located within the range of channels 500–800; thus, $a = a_1 - b$.

The 2 remaining parameters, which scale the horizontal axis of the channel number, are sought in an iterative algorithm. In examining the sum of squares of departures between the sigmoid and the spectrum, the optimal value of ChB is initially sought, assuming $s = 20$, which is a typical value. In the next step, the optimal s is located. The main calculation consists of searching for the precisely optimal ChB and s on the grid, whose density compromise the computing time and precision. The sum of squares is calculated for channels in the range (ChB – 5s, ChB + 8s). A typical result of fitting the sigmoid to the spectra is presented in Figure 6.

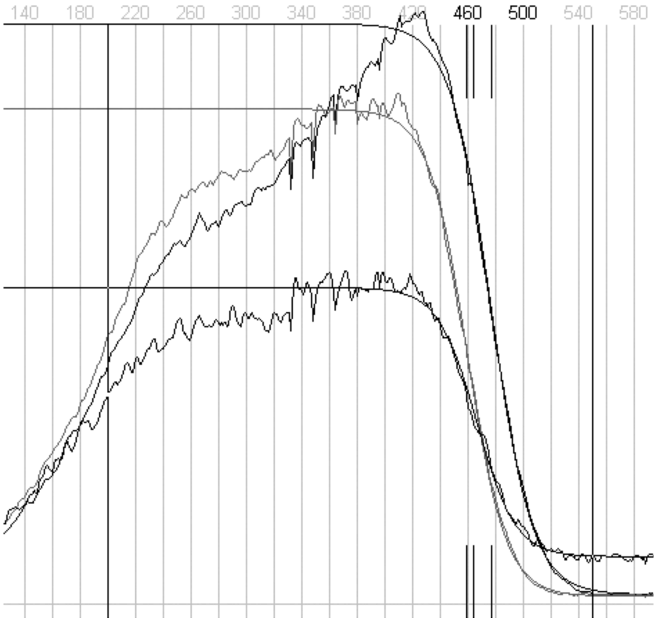

Figure 6 Two activity standards (the highest ones, despite scaled down 5 times) of ChB closest to that of the sample. The values of ChB [channel number] are 459.4 - quenched standard, 466.4 - sample, and 476.8 - unquenched standard.

The sense of the ChB parameter is visualized there also. The spectra of 501-pMC standard samples, artificially quenched (Figure 5), were used to check the linearity of the relationship between the counting rate (in the ^{14}C window) and the proposed parameter ChB. The result was $R^2 = 0.9995$, which is very good. Relatively high quenching levels are included, which results in the channel number range ChB = 360 to 480, and respective cpm range of 39 to 50. Despite this, however, nonlinearity was not detected, although it improved the regression statistics, which is also another reason for the high R^2. The obtained value is higher than the one calculated for the relationship between the counting rate and TDCR ($R^2 = 0.9981$). This means that the estimated amount of noise (unexplained variance) is almost 4 times lower for the ChB method compared to the TDCR method (however, it must be stressed that the lower limit of the 95% confidence interval for $R^2 = 0.9995$ is equal to 0.996, and is slightly below the $R^2 = 0.9981$ value).

PRACTICAL IMPLEMENTATION OF THE RIGHT-SLOPE METHOD

The algorithm for ChB parameter determination is implemented into the age calculation software. However, to be safe, the interpolation only, and not the whole regression line, is applied. For any given sample, the 2 quenched standards searched for are those closest to the sample in the sense of the ChB. In other words, 2 standards with the most similar purity level are used for the sample. The standard activity value finally used for the age determination is obtained as a result of the linear interpolation between the 2 standards.

As seen in Figure 6, it would not be easy to estimate visually the proper attenuation of the spectra, due to the different vertical ranges. At an early stage in our software development, we tried to standardize all spectra in the plot. While adequate for a general understanding of the apparatus operation, it was not very useful in practice. It is obvious that the numerical method is best. However, visualization of the calculated result by plotting the sigmoids can screen for potentially extreme cases. The procedure was tested with 21 dendrochronologically dated samples (Figure 7).

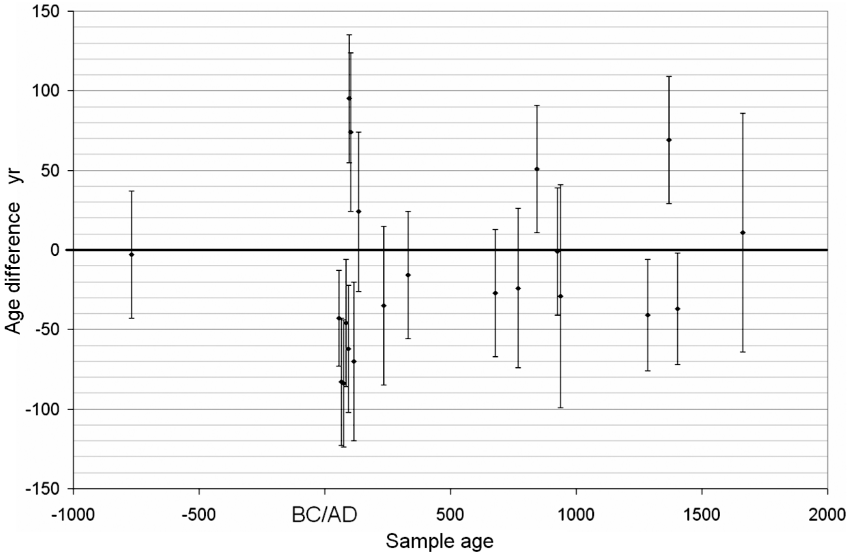

Figure 7 Difference between the measured ^{14}C age and the ^{14}C age recalculated by the calibration curve according to the sample dendrochronological age.

To estimate the statistical significance of departures presented in Figure 7, values were divided by the counting errors (indicated in the figure). The average is –0.34 ± 0.27, where the error is the standard deviation divided by $21^{1/2}$. This result clearly indicates (p value = 0.10) the absence of any bias. The standard deviation of the age differences (standardized by its Poisson errors) is 1.24 ± 0.15. The p value for testing the hypothesis that SD = 1 is equal to 0.055—meaning that the statistical null hypothesis stating that the only error is the one due to counting—cannot be rejected. However, one can say that the factor of measured to Poisson error is 1.24, which is a very good result. The Shapiro Wilk normality test, as applied to the age differences, gives a p value of 0.25.

THE QUENCHING CORRECTION BY MUON PEAK

In the right-hand side of Figure 5, there are peaks visible due to cosmic muons, independently of the ^{14}C presence in the sample but dependent on the benzene purity to the same degree as the ^{14}C pulses.

Unfortunately for the quench correction of old samples, there are considerably fewer counts here than in the ^{14}C energy range compared to the more recent samples.

The algorithm for determination of the muon peak position is similar to the one already presented, with natural modifications of the starting values. The estimated position of the right slope is denoted by ChM (channel of muons).

In order to be used for old samples, the method can be checked using active samples (Figure 5), to produce better ^{14}C counting statistics. The quality of the linear relationship of cpm to ChM is $R^2 = 0.985$, with the value apparently being inferior to the one obtained for ChB ($R^2 = 0.9995$), albeit for active samples.

The question is, for what sample activity (age) does the precision of both methods become comparable? As reviewing the many series of quenched samples of different activity would consume too much measurement time, a Monte Carlo experiment has been performed instead. The pulses (channel numbers) were generated using the accept-reject algorithm (Robert and Casella 2004). Two spectra were considered, that of ^{14}C (standard) and background. For use in the random number generator, the spectra were smoothed. Pulses are generated from the background and ^{14}C spectrum to produce the assumed percentage of modern carbon, in the range 2–110% (Figure 8). Two days of counting time is assumed. One hundred "measurements" were performed for each point to calculate the standard deviation of the obtained estimations of ChB, as well as the ChM parameter.

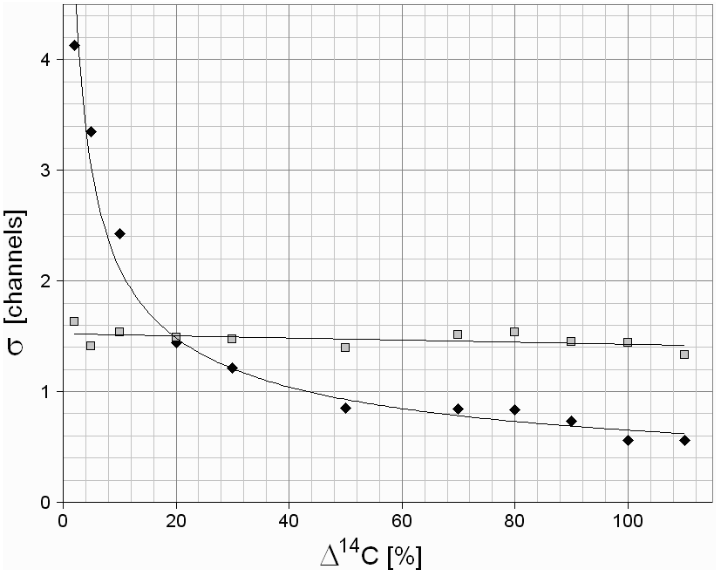

Figure 8 Precision (standard deviation, σ) of the determination of ChM (gray squares) and ChB (black diamonds), as estimated by the Monte Carlo experiment modeling 2-day measurements.

It is evident in Figure 8 that the precision of the quench correction based on the ChB falls dramatically (σ increases) with the increasing age of the sample. At $\Delta^{14}C = 20$ pMC, the precision of the channel number determinations are similar for both methods. Therefore, that point (20 pMC or 13,000 BP) seems to be the boundary for choosing whether to use ChB or ChM.

The acceptable fit of the Monte Carlo-estimated errors with the observed data point dispersion is clearly visible in Figure 9. The samples range in age from 7500 to 12,000 BP, slightly younger than the proposed 13,000 BP boundary, however, still of almost equal errors for both parameters. The age of samples is not included in Figure 9 because it indicates no meaningful pattern.

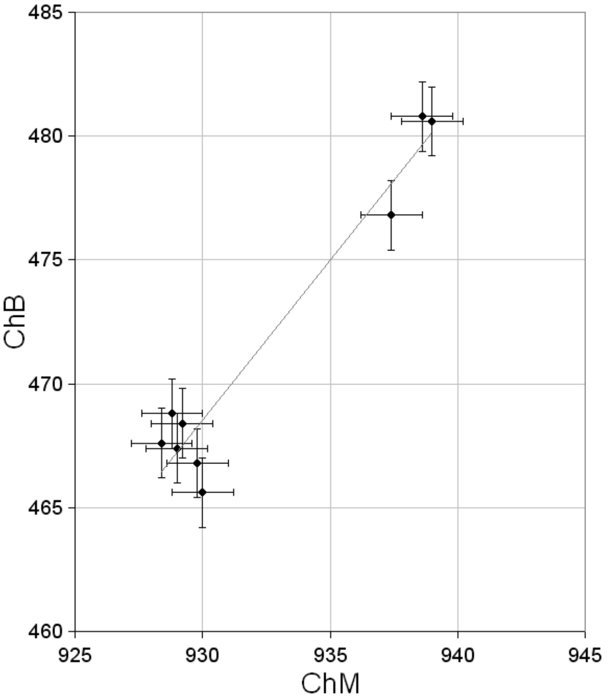

Figure 9 Correlation of the ChB and ChM parameters for a series of samples aged from 7500 to 12,000 BP. The error bars (1σ) follow the result presented in Figure 8.

CONCLUSION

The proposed method for quench correction, based on the observed position of the right slope of the ^{14}C or muons spectrum, seems to be optimal for ^{14}C dating. The Hidex 300 SL device, with the method implemented in the age calculation software, provides a robust, stable analysis. The observed 1.24 error factor and counting error of 40 yr is a good recommendation for the technology described.

REFERENCES

Broda R. 2003. A review of the triple-to-double coincidence ratio (TDCR) method for standardizing radionuclides. *Applied Radiation and Isotopes* 58(5):585–94.

Krąpiec M. 1992. Skale dendrochronologiczne późnego holocenu południowej i centralnej Polski. *Kwartalnik AGH – Geologia* 18(3):37–119.

Krąpiec M. 2001. Holocene dendrochronological standards for subfossil oaks from the area of Southern Poland. *Studia Quaternaria* 18:47–63.

McCormac FG. 1992. Liquid scintillation counter characterization, optimization and benzene purity correction. *Radiocarbon* 34(1):37–45.

Robert CP, Casella G. 2004. *Monte Carlo Statistical Methods*. 2nd edition New York: Springer-Verlag.

Simpson BRS, Meyer BR. 1994. Direct activity measurement of pure beta-emitting radionuclides by the TDCR efficiency calculation technique. *Nuclear Instruments and Methods in Physics Research A* 339(1–2):14–20.