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^{14}C DATING WITH THE ICELS LIQUID SCINTILLATION COUNTING SYSTEM USING FIXED-ENERGY BALANCE COUNTING WINDOW METHOD

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ABSTRACT. This article presents an application of a fixed-energy balance counting window in radiocarbon dating of geological peat samples. We determine a fixed-energy balance counting window with an inexpensive liquid scintillation counting ICELS system. We show long-term modern biosphere standard records that show stability sufficient for dating samples up to approximately 30,000 ^{14}C yr BP. We then compare our results to ones obtained previously using a Quantulus 1220™.

INTRODUCTION

This work is aimed to apply the semitheoretical work presented by Theodórsson (2011) into practice. Theodórsson (2011) proposed the fixed-energy balance counting window for the liquid scintillation counting (LSC) ICELS system. However, no radiocarbon dating has been reported using this method so far. Therefore, we applied the proposed system with minor modifications for ^{14}C dating of peat cores. The measurements obtained with the ICELS system are compared with previous results obtained on another LSC spectrometer, the Quantulus 1220™.

EXPERIMENTAL

LSC ICELS Systems

ICELS was designed by P Theodórsson, University of Iceland, and has been described thoroughly elsewhere (e.g. Theodórsson 2005, 2011). Therefore, just a brief description will be given here. ICELS is based on a single horizontally placed photomultiplier tube (PMT). On top of the PMT, a 7-mL low-potassium Pico™ glass vial containing LSC cocktail is placed. The LSC cocktail is composed of 2 mL of benzene and 0.026 g of butyl-PBD. The vial is wrapped with polytetrafluoroethylene (PTFE) tape and a drop of glycerol is placed between the vial and the PMT for better light collection efficiency. The counter is shielded with ~20 kg of lead. In this work, 2 ICELS systems are equipped with Tukan 8K (Guzik et al. 2006) multichannel analyzers (MCA). Despite its simple construction and low cost, ICELS provides very attractive parameters for ^{14}C dating. In the ICELS system, the quenching effect is quantified by the attenuation (A) value, defined as

$$A = \frac{C_{59.5\,\mathrm{keV}}}{C_{ref}}$$

where $C_{59.5\,\mathrm{keV}}$ is a channel number that corresponds to the 59.5-keV peak from the ^{241}Am X line of each sample, and C_{ref} is a reference channel number. The reference channel number is adjusted so that for the least-quenched samples, $A = 1.00$. Typical attenuation measured in samples varies from $A = 0.85$ up to $A = 1.00$.

Determining Fixed-Energy Balance Window

The balance counting window was first used in ^{14}C dating by Pearson (1979). Later, this same concept was used in the ICELS system (Theodórsson et al. 2003; Tudyka et al. 2010) where a balance point was set via the high-voltage adjustment. In this work, we use the multichannel analyzer

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(MCA) to set the fixed-energy balance counting window. This improves precision as it allows to include variation in the background count rate easily, and sample changing is much less time consuming because the high voltage does not need to be adjusted for each sample. Therefore, this work uses the idea presented by Theodórsson (2011) with minor modifications.

Figure 1 presents ^{14}C spectra quenched and unquenched in: a) channel and b) energy scales. On the energy scale, those spectra are almost identical, excluding low (<25 keV) and high (>156.5 keV) energy ranges. As the 2 ^{14}C spectra in the 25 to 156.5 keV energy range (Figure 1b) are almost identical, we can determine the fixed-energy balance counting window assuming linearity of the net ^{14}C spectrum. The position of the balance counting window is adjusted so that for small fluctuations (of e.g. attenuation), the count rate does not change. This balance counting window increases the overall system stability, which can be affected by e.g. high-voltage, high-temperature fluctuations (Theodórsson et al. 2003). We use the window spanning from 39.5 to 101 keV, which was chosen as a compromise between background stability, activity standard stability, and efficiency.

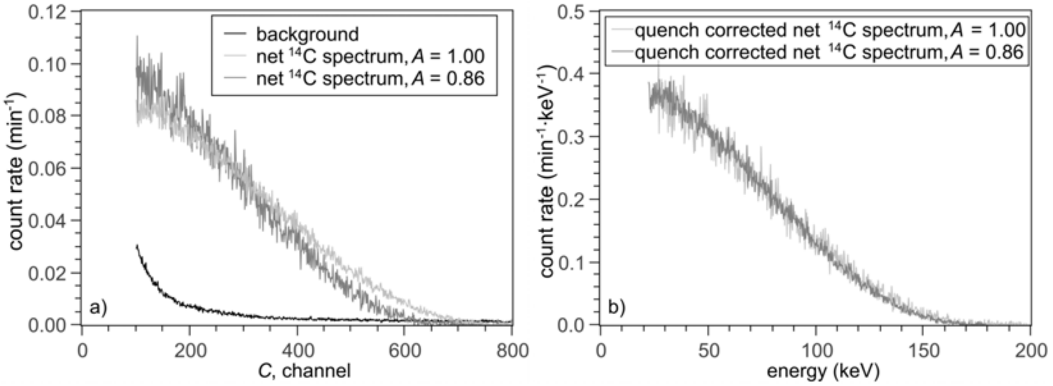

Figure 1 Background and ^{14}C ANU sucrose (quenched, unquenched) spectra in a) channel and b) energy scale measured using ICELS no. 1.

Background Count Rate Stability

The ICELS system was designed with an emphasis on simplicity. Therefore, some expensive technical solutions like active shielding were not used. This made the system sensitive to the fluctuation of cosmic radiation. Theodórsson and Gudjónsson (2009) demonstrated that the ICELS background count rate is in correlation with atmospheric pressure and therefore with cosmic radiation. This variation is especially important when old samples with count rates close to background are measured, approximately >30,000 ^{14}C yr BP. To include uncertainty larger than would be expected from Poisson statistics, we use an uncertainty multiplier. Figure 2 shows 11 measurements of background count rate as a function of attenuation. Each measurement took from 40 to 150 hr. Measurements were conducted over 10 months and lasted for 28 days in total.

Modern Biosphere Count Rate Stability

Figure 3 shows 9 measurements of modern biosphere standard count rate. Each measurement took from 40 up to 220 hr. The modern biosphere standard count rate was determined using IAEA C-6, also known as ANU sucrose. The IAEA C-6 secondary standard has 150.61% of modern biosphere activity (Różański et al. 1992). Measurements were conducted over 10 months and lasted for 41 days in total and were fully stable. The net count rate was calculated after subtracting the quench-

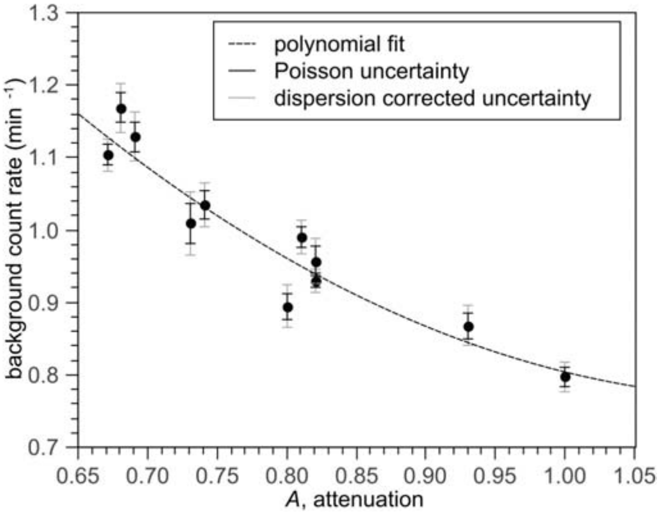

Figure 2 Background count rate as a function of attenuation. Error bars correspond to Poisson and dispersion-corrected uncertainty. Measurements were performed using the ICELS no. 1 system.

corrected background (Figure 2) for each individual fixed-energy balance window position. The net count rate was normalized to the modern biosphere activity and to δ^{13}C according to Stuiver and Polach (1977) and Polach (1979). Some of the ANU sucrose samples were artificially quenched by the addition of a small amount of acetone. The calculated modern biosphere count rate in Figure 3 is 9.452(12) min^{-1}. A rough estimation gives 10 ^{14}C yr of uncertainty originating from the radioactivity standard. For ^{14}C dating, this uncertainty needs to be combined with the statistical count rate uncertainty of the measured sample.

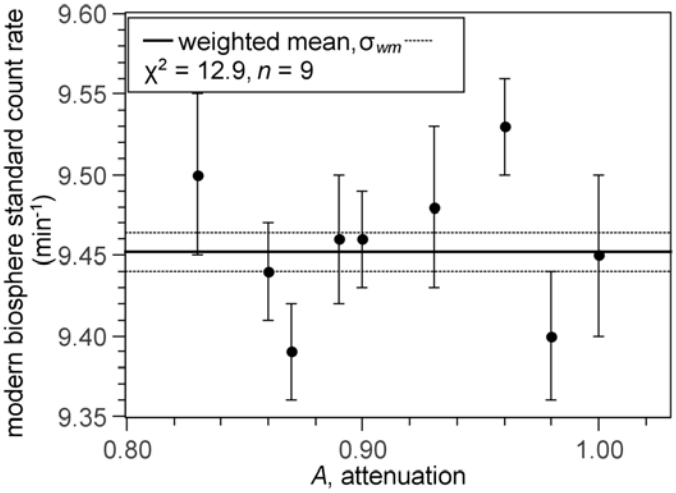

Figure 3 Modern biosphere standard count rate determined using IAEA C-6 secondary ^{14}C standard as a function of attenuation. Measurements were performed using the ICELS no. 1 system.

^{14}C DATING

Sample Description and Preparation

The sampled peat core was collected near Żyglin (southern Poland). A detailed site description was given by Tudyka and Pazdur (2010). The peat spans a 2-ha area and is situated near the drainage of the Brynica River. Due to the 20-cm sand layer covering the surface, the peat was well preserved to the present day. The peat contains large amounts of charcoal, copper, lead, silver, and zinc. It is highly suspected that their presence is related to early metallurgical smelting in this region.

Samples were treated with the standard acid-alkali-acid procedure to remove humic acids, chitin, fungal products, etc. Benzene for the LSC cocktail was produced using standard methods in the GADAM Centre (Pawlyta et al. 1998). Before measurement, samples were stored for over 1 month to allow all ^{222}Rn and daughter isotopes to decay.

Results Comparison

Table 1 presents the results obtained with the 2 ICELS systems and the Quantulus 1220. The ^{14}C age was calculated according to Stuiver and Polach (1977) and Polach (1979). To compare the results obtained on 3 LSC spectrometers, we use the difference between the weighted mean (Figure 4) calculated for 16 samples ^{14}C dated with 3 spectrometers.

Table 1 ^{14}C dates of a peat profile from the Żyglin site using 3 different spectrometers.

Depth (cm)	Spectrometer	Lab nr	Age (^{14}C yr BP)
20–21	Quantulus 1220 no. 2	GdS-759	1410 ± 55
22–23	ICELS no. 2	GdC-244	1270 ± 130
28–29	ICELS no. 1	GdC-565	1560 ± 40
	ICELS no. 2	GdC-564	1565 ± 50
	Quantulus 1220 no. 2	GdS-848	1660 ± 50
29–30	ICELS no. 1	GdC-563	2045 ± 70
	ICELS no. 2	GdC-566	2030 ± 50
	Quantulus 1220 no. 2	GdS-849	1990 ± 65
31–32	ICELS no. 1	GdC-419	1755 ± 70
	ICELS no. 2	GdC-418	1795 ± 75
	Quantulus 1220 no. 2	GdS-850	1830 ± 55
34–35	ICELS no. 1	GdC-557	2310 ± 160
	ICELS no. 2	GdC-556	2230 ± 200
	Quantulus 1220 no. 2	GdS-859	2210 ± 150
40–41	ICELS no. 1	GdC-561	2715 ± 50
	ICELS no. 2	GdC-560	2720 ± 40
	Quantulus 1220 no. 2	GdS-858	2915 ± 55
42–43	ICELS no. 1	GdC-569	2770 ± 70
	ICELS no. 2	GdC-572	2870 ± 55
	Quantulus 1220 no. 2	GdS-834	2910 ± 50
44–45	Quantulus 1220 no. 2	GdS-851	3315 ± 50
50–51	Quantulus 1220 no. 2	GdS-830	3695 ± 50
57–58	ICELS no. 1	GdC-417	3960 ± 70
	ICELS no. 2	GdC-420	3780 ± 50
	Quantulus 1220 no. 2	GdS-835	3865 ± 50
63–64	ICELS no. 1	GdC-409	4400 ± 100
	ICELS no. 2	GdC-412	4500 ± 55
	Quantulus 1220 no. 2	GdS-763	4445 ± 90

Table 1 ^{14}C dates of a peat profile from the Żyglin site using 3 different spectrometers. *(Continued)*

Depth (cm)	Spectrometer	Lab nr	Age (^{14}C yr BP)
64–65	ICELS no. 1	GdC-411	4550 ± 110
	ICELS no. 2	GdC-410	4590 ± 50
	Quantulus 1220 no. 2	GdS-763	4435 ± 65
73–74	Quantulus 1220 no. 2	GdS-873	6945 ± 70
79–80	ICELS no. 1	GdC-237	8300 ± 130
	ICELS no. 2	GdC-570	8130 ± 70
	Quantulus 1220 no. 2	GdS-874	8340 ± 75
82–83	Quantulus 1220 no. 2	GdS-884	9265 ± 70
85–86	ICELS no. 1	GdC-243	9120 ± 80
	Quantulus 1220 no. 2	GdS-875	9320 ± 80
89–90	ICELS no. 1	GdC-559	9570 ± 110
	ICELS no. 2	GdC-562	9460 ± 100
	Quantulus 1220 no. 2	GdS-876	9740 ± 110
92.5–95	ICELS no. 1	GdC-431	9950 ± 100
	ICELS no. 2	GdC-430	9600 ± 200
	Quantulus 1220 no. 2	GdS-1054	10,090 ± 140
100–102.5	ICELS no. 1	GdC-429	9890 ± 120
	ICELS no. 2	GdC-432	9740 ± 65
	Quantulus 1220 no. 2	GdS-1055	9785 ± 110
110–112.5	ICELS no. 1	GdC-478	10,100 ± 100
	ICELS no. 2	GdC-479	10,110 ± 95
	Quantulus 1220 no. 2	GdS-1057	9950 ± 120
115–117.5	ICELS no. 1	GdC-555	10,710 ± 190
	ICELS no. 2	GdC-558	10,525 ± 55
	Quantulus 1220 no. 2	GdS-1057	10,210 ± 110
120–122.5	ICELS no. 1	GdC-477	10,620 ± 100
	ICELS no. 2	GdC-580	10,640 ± 65
	Quantulus 1220 no. 2	GdS-1058	10,660 ± 110
125–117.5	Quantulus 1220 no. 2	GdS-896	10,880 ± 110[a]

[a] Sample age is 1160 ^{14}C yr younger than the result published earlier by Tudyka and Pazdur (2010). This error was eliminated after noticing a systematic decrease of the standard count rate caused by a sample elevator breakdown in the Quantulus 1220.

Independently, we performed a χ^2 test to verify the agreement of the results. The χ^2 values for ICELS no. 1, ICELS no. 2, and Quantulus no. 2 versus the weighted mean are 9.6, 8.2, and 20.0, respectively. It is likely that small values of χ^2 for ICELS systems are the consequence of including background variation. The samples on ICELS were measured in pairs; hence, the background count rate was slightly systematically shifted. This factor may be responsible for the small systematical difference.

Age-Depth Models

^{14}C dates were calibrated to calendar ages using the IntCal09 calibration curve (Reimer et al. 2009). Age-depth models were made with the OxCal v 4.1.7 program (Bronk Ramsey 2008) using the P_Sequence (Bronk Ramsey 2009) function. The *k* parameter of the P_Sequence, which describes increments per unit length of core, was set to 1 cm^{-1}. Figure 5 presents 2 age-depth models obtained for a) the Quantulus 1220 no. 2 and b) the weighted mean of ICELS no. 1 and no. 2. The 2 age-depth models are very similar, although there are differences caused mostly by the fact that not every sample was dated using all 3 LSC systems.

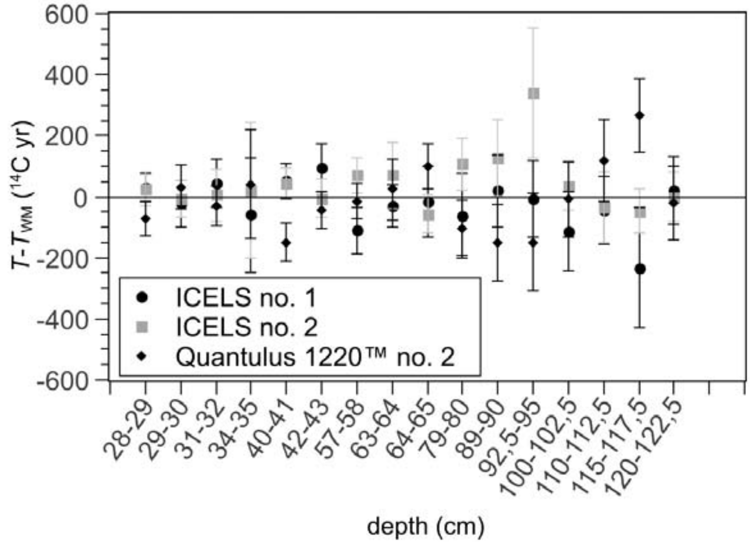

Figure 4 Difference of ^{14}C age (T) and weighted mean (T_{WM}) for ICELS no. 1, ICELS no. 2, and Quantulus 1220 no. 2 versus sample depth.

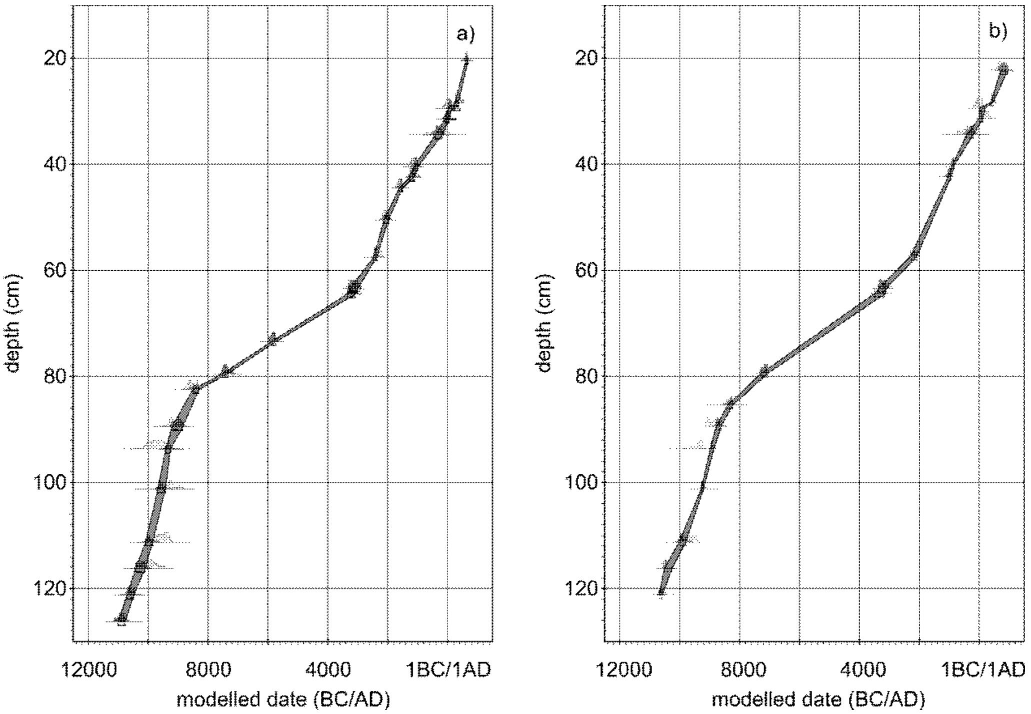

Figure 5 Age-depth models obtained with a) the Quantulus 1220 no. 2 and b) the weighted mean of ICELS no. 1 and 2. The gray curve represents the 68% highest probability density range. Distributions for the single calibrated dates are marked with light gray. Posterior distributions are marked with dark gray and take into account the depth model.

CONCLUSIONS

Background and the modern biosphere secondary standard count rate are sufficiently stable for accurate ^{14}C dating using ICELS. The overall system stability is very good, proving that ICELS can be used for accurate and precise ^{14}C dating of samples up to ~30,000 ^{14}C yr old. The results obtained on 2 ICELS systems and the Quantulus 1220 are in agreement, although a negligible systematical difference is noted between the ICELS and Quantulus 1220.

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