

## A SIMPLE, EXTREMELY STABLE SINGLE-TUBE LIQUID SCINTILLATION SYSTEM FOR RADIOCARBON DATING

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**ABSTRACT.** This paper describes a simple and compact liquid scintillation radiocarbon dating system, ICELS, and demonstrates its long-term stability and reproducibility to a precision level rarely presented before, better than 0.04% ( $3^{14}\text{C}$  yr). Inexpensive systems of this kind may, in the future, help to meet increasing demand for high precision ( $\pm 16$  to  $\pm 20^{14}\text{C}$  yr) and strict quality control. ICELS comprises a compact detector unit, where a 3-mL dome-shaped vial, with an optimal light reflector, sits on the top of a vertical 30-mm photomultiplier tube. Sample changing is manual. The high voltage is set at the balance point for each sample, securing maximal counting stability. The quench correction method used (spectrum restoration) corrects with 0.04% precision for all parameters that can normally shift the  $^{14}\text{C}$  spectrum. For 3 mL of benzene at 71%  $^{14}\text{C}$  counting efficiency (recent carbon 23 cpm), the background is 1.72 cpm behind a 5-cm-thick shield of lead (27 kg) and 1.53 cpm behind 10 cm of lead. The background count rate corrected for atmospheric pressure variations was completely stable over 47- and 57-d testing periods for the 2 systems.

### INTRODUCTION

Liquid scintillation (LS) counting has been the preferred method of radiometric radiocarbon dating laboratories established during the last 3 decades. The systems used today are nearly all based on the 2-photomultiplier tube (PMT) coincidence technique, and were originally designed for biomedical tracer studies where a variety of radioisotopes of wide energy and quench level range are measured. Since the mid-1980s, low-level systems of similar type but redesigned or modified for low-level counting, have been produced (Kojola et al. 1984; Noakes et al. 1989) and are now preferred in  $^{14}\text{C}$  dating despite their higher price.

From the beginning of high-precision ( $\pm 16$  to  $\pm 20^{14}\text{C}$  yr) LS dating in the 1970s until the early 1990s, high precision was mainly reserved for the establishment of the dendrochronological  $^{14}\text{C}$  time scale. Today, this precision, together with strict quality control, is increasingly applied to archaeological studies requiring long counting times, which, for economic reasons, may be difficult to meet. This paper describes a new laboratory-built system, ICELS, which is radically different from modern commercial LS systems, as simplicity, compactness, and ease of use in  $^{14}\text{C}$  dating has been emphasized in its design. Systems of this kind may, in the future, help to secure sufficient counting capacity in high-precision dating.

The main aim in designing ICELS has been to use it to solve the dilemma of the earliest Norse settlement in Iceland (Theodórsson 1998).  $^{14}\text{C}$  dating strongly indicates that settlement occurred about 150 yr earlier than previously thought. These results have been rejected as archaeologically unacceptable by Icelandic archaeologists and historians. High-precision dating of 50–100 samples can presumably resolve this serious dilemma.

### NEW DESIGN PREREQUISITES

ICELS differs from modern commercial LS counting systems in various respects, as the latter have some features that are superfluous in  $^{14}\text{C}$  dating. The main features of ICELS and differences from conventional systems are the following:

1. A single 30-mm-diameter PMT replaces the dominating 2-tube (50 mm diameter) coincidence arrangement, resulting in a simple and compact detector unit. This greatly reduces the dimensions and the weight of the system.

2. Replacing the 2 tubes with 1 smaller tube reduces the beta and gamma radiation the vial is exposed to from natural radioactivity in the glass bulb of the PMT, lowering the background.
3. A 3-mL dome-shaped vial with an optimal light reflector, sitting on the top of the vertical PMT, secures high photon collection at the cathode.
4. Modern LS systems have a built-in pulse height analyzer with 2000 channels or more. In ICELS, it is replaced by 4 counting channels, sufficient for high-precision dating, as demonstrated by Pearson (1979, 1983) in his pioneering dendrochronological work.
5. A logarithmic amplifier is advantageous when radioisotopes of wide energy and quench range are measured. In  $^{14}\text{C}$  dating, a linear keV calibrated energy scale is more appropriate, with counting window limits given by a basic physical unit (keV) rather than by an instrument-dependent parameter.
6. Benzene dating samples are usually quenched to some degree. The high voltage is set at the balance point of each sample, which secures maximal stability of counting efficiency and minimizes the quench correction needed. In conventional systems, all samples are counted at the same high voltage, irrespective of quench level.
7. The simplicity of the electronic unit enhances reliability and makes maintenance easier.
8. Automatic changing of 200 samples or more, which significantly increases the size and price of conventional systems, is indispensable in tracer work, where a large number of samples are measured. In  $^{14}\text{C}$  dating using a stable system, ICELS offers little advantage, as counting periods are generally 2 d or more. Therefore, ICELS has manual sample changing.

Regarding the last point, there is a widespread belief that automatic cyclic measurements of a number of unknown, standard, and background samples, usually extending 2 weeks or more, increases accuracy (Gupta and Polach 1985). G W Pearson, using a late-1960s LS system with 4 fixed counting windows, demonstrated that the count rate of both background and standard samples was, after appropriate corrections, constant for several years (Pearson 1983). Therefore, cyclic counting adds nothing to the precision when the system is operated in a balance counting mode.

### THE NEW LS SYSTEM, ICELS

ICELS was designed and built at the Science Institute specifically for  $^{14}\text{C}$  dating. It is based on earlier development work in Iceland (Einarsson 1992; Einarsson and Theodórsson 1995). ICELS comprises a shielded detector unit (27 kg with an economical 5-cm-thick shield of lead); a compact, dedicated electronic unit ( $32 \times 25 \times 9 \text{ cm}^3$ ); and a laptop computer, which controls the counting operations and processes the signals. The simplicity of the electronic unit and the resulting simplicity in data recording have been emphasized.

A specially made dome-shaped 3-mL quartz vial sits on top of a vertical 30-mm-diameter PMT, touching the tube but without optical coupling (Figure 1). The vial is wrapped (a process taking 2 min), except for its bottom, with 2 layers of a thin teflon tape, which provides high light reflection. This simple arrangement results in a closed vial/phototube geometry, with high collection of the scintillation photons at the PMT cathode. The samples are 3 mL of benzene to which 45 mg butyl-PBD is added.

The electronic unit of ICELS is quite simple. It has a dedicated linear amplifier of modest speed, as only moderately sized pulses need to be detected. The PMT can thus be operated at lower voltage than when a conventional LS system is used, where single cathode electron pulses need to be detected. The amplified pulses are sent in parallel to 4 pulse height discriminators, D1 to D4, which are triggered when an input pulse overrides their individually set threshold voltages, DV1 to DV4, produced by a fixed resistor chain. The discriminators are read by the computer, and when one or

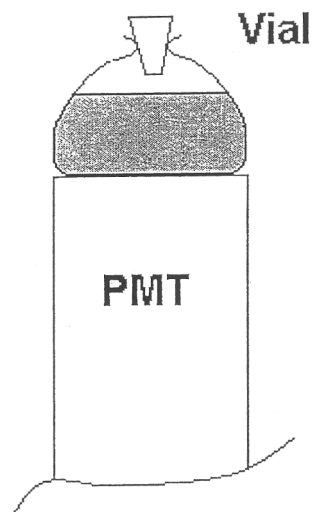


Figure 1 A schematic figure of the detector unit

more have been activated, one count is added in the respective computer internal pulse-summing registers, N1 to N4.

The discriminator voltages DV1 and DV3 define the lower and upper limits of the  $^{14}\text{C}$  window. The number of pulses in this window,  $N(^{14}\text{C})$ , is therefore:

$$N(^{14}\text{C}) = N1 - N3 \quad (1)$$

Discriminator voltages of D2 and D4 are set at  $0.44 \times \text{DV3}$  and  $1.25 \times \text{DV3}$ , respectively, and are used to facilitate the setting of the high-voltage balance point, as described below.

#### DETERMINING $^{14}\text{C}$ BALANCED SETTING

To secure the highest stability of counting efficiency, the system is operated in a balanced counting mode (McCormac 1992; Theodórsson et al. 2003,) where the PMT high voltage is set at a value that gives a maximum count rate in a fixed  $^{14}\text{C}$  window for an unquenched sample. The discriminator voltage ratio DV3/DV1 determines explicitly the balanced window limits as well as the counting efficiency, and these will be exactly the same for any similar LS system with the same discriminator voltage ratio and similar light collection. Figure 2 shows the lower and upper limits (keV) of a balanced window as a function of the discriminator voltage ratio DV3/DV1 (Theodórsson et al. 2003).

When selecting a  $^{14}\text{C}$  window, its lower energy limit is usually set above the maximum energy of tritium beta particles (18 keV). A discriminator ratio of 5.37 was selected, resulting in a  $^{14}\text{C}$  counting window from 25.4 to 136 keV, as the background rises rather steeply below the lower window limit (Figure 3). Figure 4 shows the  $^{14}\text{C}$  spectrum at balanced high voltage and the channels corresponding to the 4 discriminators. The detection efficiency in the  $^{14}\text{C}$  counting window is 71%.

The balanced PMT high voltage for the selected fixed  $^{14}\text{C}$  counting window was determined by measuring an unquenched high-activity  $^{14}\text{C}$  benzene sample (about 200 Bq) in steps of increasing PMT high voltage. Figure 5 shows the count rate in the  $^{14}\text{C}$  window as a function of high voltage. It goes through a maximum at a voltage value called balance point, denoted by  $HV_{bal}$ . Determining the balance point of a single-PMT system is considerably simpler than for conventional 2-PMT systems (McCormac 1992).

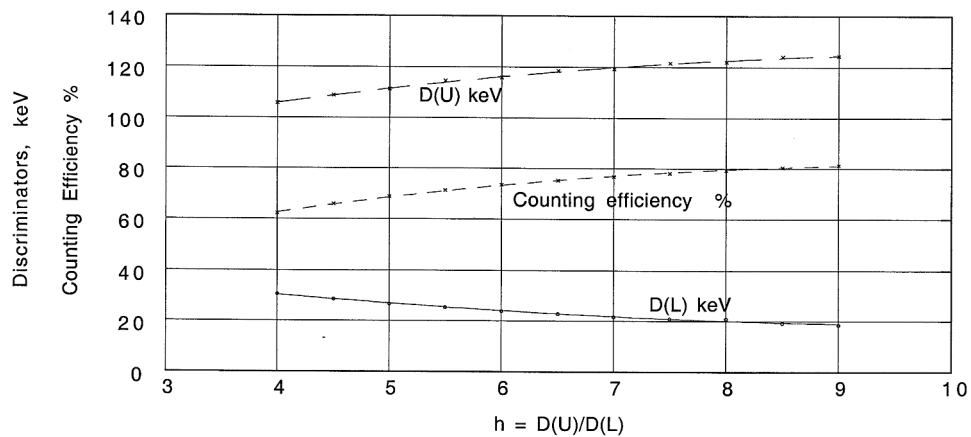


Figure 2 Lower [D(L)] and upper limit [D(U)] (keV) of a balanced window versus ratio of upper and lower discriminator voltage.

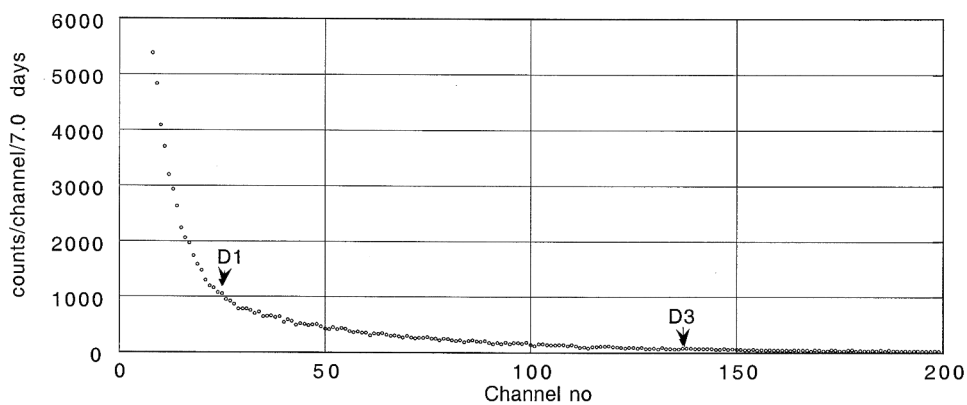


Figure 3 Background pulse height spectrum

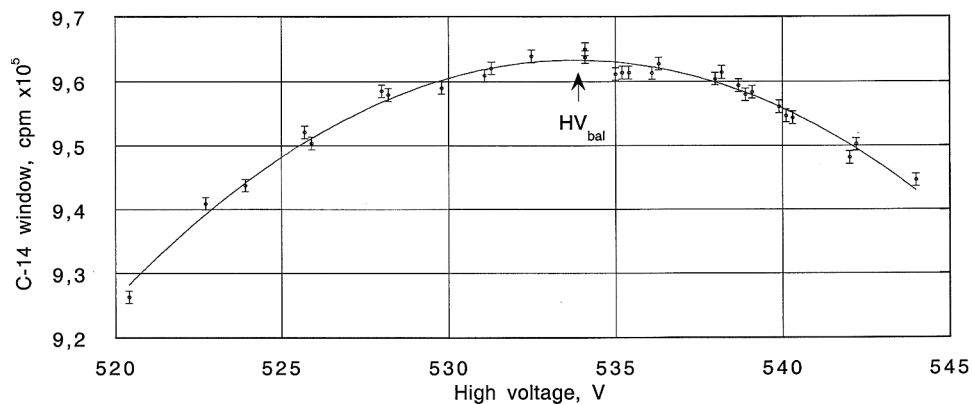


Figure 4 Pulse height spectrum of <sup>14</sup>C. Error bars are shown on day 41.

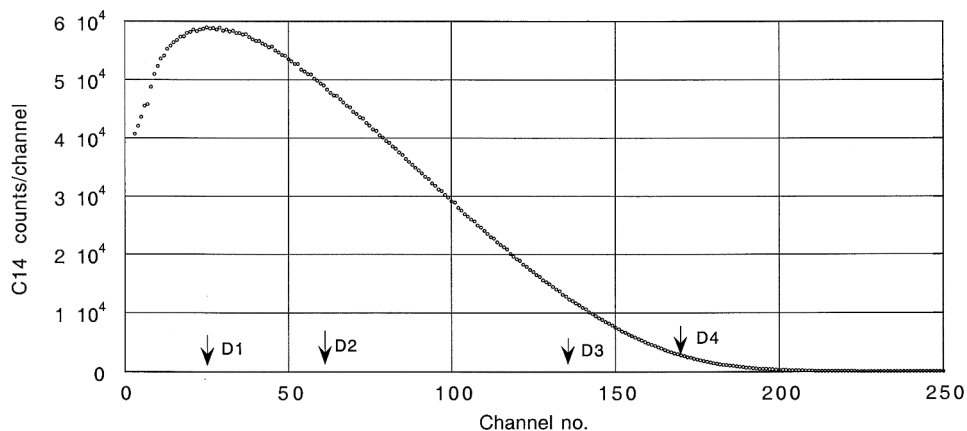


Figure 5 <sup>14</sup>C count rate versus high voltage

**SETTING BALANCED HV FOR DATING SAMPLES**

Small impurities in synthesized benzene dating samples shift the <sup>14</sup>C pulse height spectrum to lower pulse size and changes the counting efficiency compared to the unquenched reference sample. A measure of this shift can be determined by the conventional channel ratio method. An <sup>241</sup>Am gamma (60 keV) source is inserted close to the vial and counted for about 5 min. The channel ratio *AM* defined by

$$AM = (N2 - N3) / (N1 - N3) \tag{2}$$

is sensitive to spectrum shift.

<sup>241</sup>Am has been selected because its gamma energy lies in the energy range of the beta particles of <sup>14</sup>C. For ICELS, the reference sample has an *AM* value of 0.49 at the balance point. If *AM* for a sample to be dated deviates from 0.49, the high voltage is adjusted to a value that sets *AM* to this balance value, which restores the spectrum to the same position as that of an unquenched reference sample. A separate quench correction study that will be published in the near future shows that the error due to quench correction can be kept below 4 <sup>14</sup>C yr.

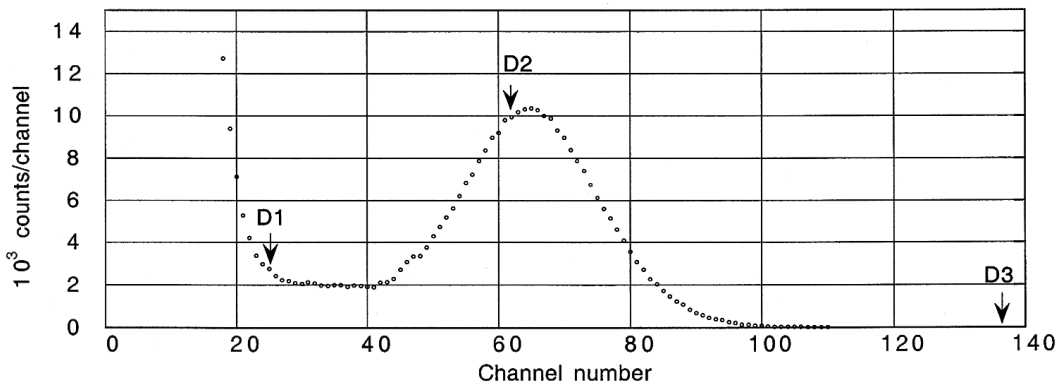


Figure 6 Pulse height spectrum of an external <sup>241</sup>Am source

## COUNTING STABILITY OF ICELS

The long-term counting stability of ICELS has been studied in detail, as well as the influence of all parameters that affect the counting efficiency.

### Influence of Power Line Voltage

Using an external multichannel pulse height analyzer, the channel number of the middle of the 60-keV peak of  $^{241}\text{Am}$  was determined at a line voltage of 200, 220, and 240 volts. The peak channel number varied by less than 0.3%, which is similar to the measuring error. Line voltage variations evidently have a negligible effect on the counting efficiency.

### Influence of Ambient Temperature

Because of the high internal stability of amplifier gain and high voltage, any likely temperature variations in the electronic unit should have a negligible effect on the  $^{14}\text{C}$  spectrum. This was tested as above at varying temperatures of the electronic unit, from 13 °C to 33 °C, measured in 7 approximately equal steps. The channel number of the  $^{241}\text{Am}$  60-keV peak was practically the same at all temperatures, with a 0.3% rms deviation from the mean channel number, similar to the estimated measuring error.

The detector unit is, however, quite sensitive to temperature variations, as the internal gain of the PMT decreases linearly by 0.46% per °C (Theodórsson et al. 2003). When a sample is initially set at its balance point, a drift of 8 °C from the initial temperature will change the counting efficiency by only 0.1%. Therefore, it should not be difficult to keep the error, due to this source, within acceptable limits during the counting period of each sample, generally 1 to 7 d.

### Long-Term Stability of Counting Efficiency

In a general stability study of ICELS, extending over 110 d, a high-activity  $^{14}\text{C}$  benzene sample (about 170 Bq) was measured periodically for 16 to 24 hr. Between counting periods, the vial was removed from the detector unit and other test measurements were made. Twice the sample was measured, several days unattended, and 24-hr readings recorded. The results of all these measurements (Figure 7) show the system's excellent long-term counting stability and reproducibility in sample changing. The slow, linear decline in the count rate is due to a small, constant evaporation loss, verified by weighing the vial accurately a few times during the testing period. The standard deviation of the measured points from the line is 0.036% (corresponding to 2.9  $^{14}\text{C}$  yr), practically the same as the uncertainty due to counting statistics in individual daily-measured values, 0.034%.

In a later 26-d continuous test, with a higher-activity  $^{14}\text{C}$  sample (872 cps) showing no benzene loss, the 24-hr mean values of the count rate gave a standard deviation of 0.013% (corresponding to 1.0  $^{14}\text{C}$  yr). The expected standard deviation due to statistics is practically the same, 0.012%.

### Correction for Quenching and Other Parameters That Can Shift the $^{14}\text{C}$ Spectrum

Impurity molecules in synthesized benzene samples absorb light, resulting in fewer photons falling on the cathode of the PMT, thus shifting the  $^{14}\text{C}$  spectrum to lower energies. Other parameters can shift the  $^{14}\text{C}$  spectrum: variation in sample volume (from 1.0 to 3.0 mL), eccentric positioning of the vial on the PMT, and variation in vials and light reflection. It will be shown in a future paper that a shift in  $^{14}\text{C}$  counting efficiency due to variation in all these parameters is corrected for by the quench correction method, described briefly above (spectrum restoration), with an error less than 0.04% (3.2  $^{14}\text{C}$  yr).

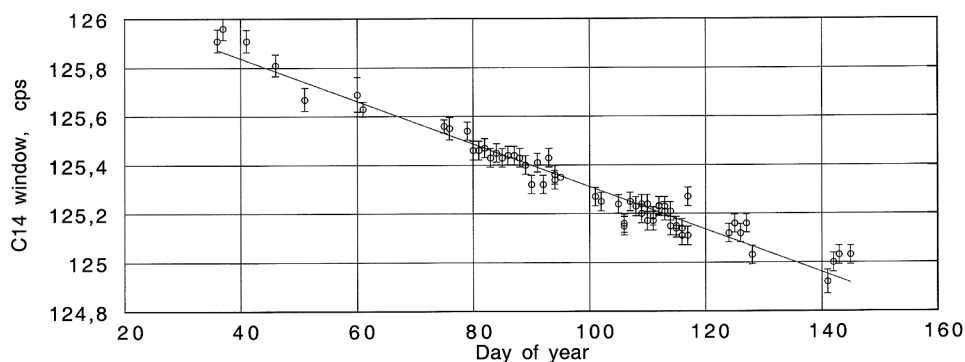


Figure 7 Count rate with 1- $\sigma$  error bars of a high-activity  $^{14}\text{C}$  benzene sample measured periodically for 16 to 24 hr over a period of 110 d.

### Replacing PMT

The count rate of a high-activity sample was measured with 3 types of 30-mm-diameter PMTs after the system had been set at the balance point for each tube. Two different tubes were measured for 1 type (D842) and 1 tube was tested twice. The counting time was 24 hr, resulting in a standard statistical deviation of 0.009 cps (0.13%). The rms deviation from the mean of the 6 measurements (Figure 8) is 0.007 cps. Exchanging PMTs, or using another ICELS for that matter, therefore gives no measurable change in counting efficiency—further evidence for the excellent counting efficiency stability. Thus, it is easy to produce systems with exactly the same counting efficiency.

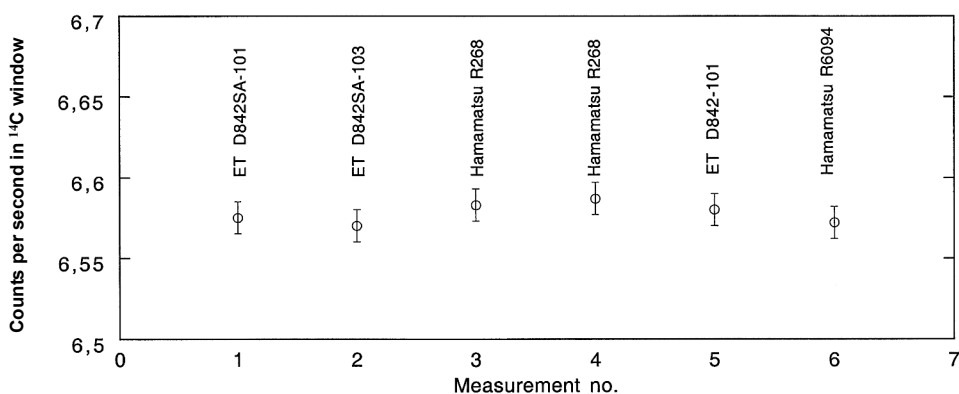


Figure 8 The count rate of a  $^{14}\text{C}$  standard for different PMTs

### Background Stability

The long-term stability of the background count rate of LS dating systems has generally been tested by measuring the background repeatedly in 100-min periods. This is far from satisfactory, since the background must be measured in periods with similar length as normal counting time of dating samples in order to reveal eventual small but significant fluctuations. Therefore, the background was measured of 2 ICELS systems (Table 1) continuously for 57 d and 47 d, respectively (Figure 9).

PMT D842SA was specially manufactured in 2002 with a bulb of newly developed high-purity glass and D190XSA was manufactured in 1990 from the best available glass at that time. Both types were made specially by Electron Tubes Limited (UK) for this low-level work. The higher background in system Fe is due to a lighter shield and higher K/Th/U concentrations in the glass bulb of the PMT.

Table 1 Systems used for background measurements.

System	Shield	PMT	Production year	Vial nr	Background cpm
Pb	10 cm lead	D842SA	2001	13	1.53
Fe	10 cm iron	D190XSA	1991	12	3.37

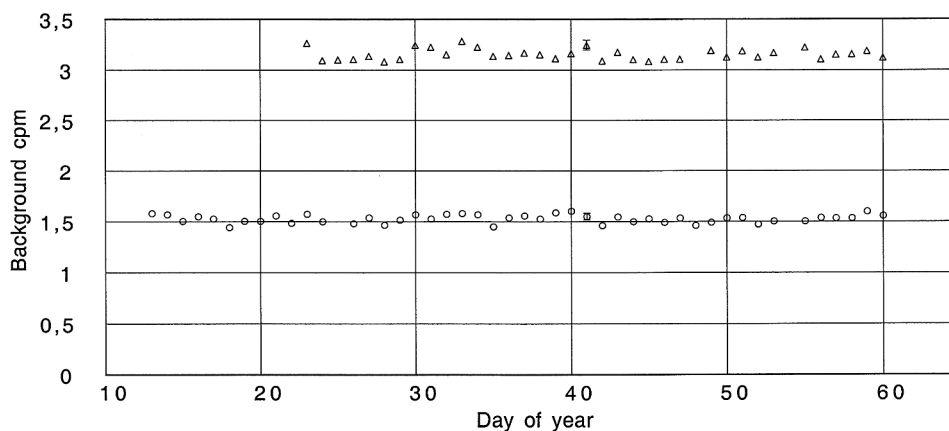


Figure 9 Long-term 24-hr average values of background count rate for 2 ICELS systems (see Table 1). For clarity, the standard error is only shown on 1 point in each series.

From the data (6-hr counting periods), 24-hr and 4-d average background values were calculated. The background depends linearly on atmospheric pressure; an increase in pressure reduces the background. From the daily average values of background and atmospheric pressure, the linear correlation factor  $\Delta B/\Delta P$  (cpm/100 mbar) was calculated and used to find the corrected background values, both for the 24-hr and 4-d mean values (Table 2). The root mean square ( $\sigma$ , rms) deviations of the average corrected background values have been calculated as well as the theoretical rms values, based on the statistical nature of the background pulse rate (Table 2).

Table 2 Long-term background measurements, corrected for variations in atmospheric pressure.

System	$\Delta B/\Delta P$ cpm/100 mb	$\sigma$ 24-hr measured cpm	$\sigma$ 24-hr expected cpm	$\sigma$ 4-d measured cpm	$\sigma$ 4-d expected cpm
Pb	-0.010	0.0042	0.0032	0.0022	0.0016
Fe	-0.012	0.0042	0.0047	0.028	0.024

The result shows that the measured  $\sigma$  for both systems is only slightly larger than the statistically calculated values, even for the 4-d averages. The corrected 4-d background is practically constant over the long testing period.



## CONCLUSION

A simple and compact single-PMT liquid scintillation counting system, specifically designed for  $^{14}\text{C}$  dating, has been built and tested to higher precision (0.03–0.04%) than that reported for any similar system. Sample changing is manual. The total weight of the instrument is 30 kg. The stability of its counting efficiency, including quench correction and sample changing, is better than 0.04%. The background is 1.53 cpm when the detector unit is shielded by 10 cm of lead, and 1.73 cpm in a 5-cm-thick shield weighing 27 kg. Systems of this type may, in the future, greatly facilitate high-precision dating.

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