LOW-LEVEL LIQUID SCINTILLATION SPECTROMETER FOR β-COUNTING

H. KOJOLA[1], H. POLACH[2], J. NURMI[1], A. HEINONEN[1], T. OIKARI[1] and E. SOINI[1]

[1] Research Department, Wallac Oy, P.O. Box 10, SF-20101 Turku
[2] Radiocarbon Dating Research, Australian National University, P.O. Box 4, Canberra 2600

Abstract

A new liquid scintillation (LS) spectrometer has been developed. It improves the signal to noise ratio of C-14 assays by an order of magnitude compared to conventional LS systems. As a result, precision for a modern sample is 0.2 % and the dating limit is 64 Ky BP for a 15 ml sample of benzene. Sophisticated MCA facilities allow the use of *Multiparameter Multichannel Analysis* for data validation and age evaluation. Despite the high sophistication, the spectrometer, (named *QUANTULUS*) is self contained, microprocessor controlled and user friendly. It can be used with full advantage in a normal laboratory environment.

Introduction

Critical assays of C-14 content of sample to be dated must evaluate all sources of error affecting overall accuracy of the method. Limiting factors which can be defined are: 1. Precision of C-14 countrate determination 2. Inherent errors: (i) C-14 half-life (ii) C-13/C-12 isotopic fractionation (iii) error associated determination of C-14 content of modern reference standard (iv) variation of past C-14 production rates (v) non uniformity of distribution of C-14 in nature and (vi) recent changes of C-14 concentration in the atmosphere 3. Contamination 4. Biological age of material to be dated 5. Association of sample and event to be dated 6. Human errors in field and laboratory and 7. Interpretation or results (Polach, 1975).

The limiting factors 2 to 7 can be minimised by good field and laboratory practices and by interpretation of results. Only the factor 1 is based on physical measurements (counting of C-14 decays by gas-proportional or liquid scintillation spectrometry; or counting of C-14 itotopic species by accelerator masspectrometry). Libby thus deliberately chose to quote age determinations and their errors based only on measurement of residual C-14 in the sample (Libby, 1946). This is the practice even today.

International crosschecking of results based on the 'same' sample has vividly demonstrated that variable results were due to factors as defined by points 2 to 7 above (Polach, 1972; Currie and Polach, 1980). However, results of a recent interlaboratory comparison were interpreted by Scott and Baxter (1980) as also showing a bias depending on counters used. It was then stated that the gas-proportional counting technique scored better than liquid scintillation counting.

In this article we shall describe a liquid scintillation spectrometer and give results obtained by it that demonstrate that the precision of the liquid scintillation counting method can be equal to that achieved by the world's very best gas proportional systems (Mook, 1983).

The Counter

A special purpose, low-level, high precision liquid scintillation spectrometer was developed and named *Quantulus** (registered trade mark, LKB-Wallac, Finland). The Quantulus is a multiparameter multichannel spectrometer enabling the simultaneous acquisition of two independent 2048 or four different 1024 pulse height (energy) spectra (Kojola, Polach, et al., 1984; Polach, Kojola, et al., 1984). These spectra are processed by an inbuilt microcomputer and dumped to an external computer (eg. the optional personal computer, PC) using especially developed software.

The software enables user selected sequencing of a series of unknown samples (U), background (B) and reference standard (S) at a cycle frequency and duration defined by the required precision of countrate determinations. If U, B and S are cycled at relatively short intervals, relative to the cumulative counting time, this leads to the *Quasi Simultaneous* (QS) data acquisition (Polach, 1969, 1974) and its validation, based on statistical analyses, by the inbuilt QS software.

60 random access counting positions are available. In principle, full log-energy spectra spanning not only the C-14 region of interest (1—156 keV) but higher energies (up to 2 MeV) can always be monitored for all counting positions by the multichannel analysers (MCAs). Thus not only the interfering species of H-3 (low energy) but of Radon (high energy) is readily identified. Suspect spectra can be compared to master spectra and false result reporting is avoided. Whilst the PC stores all data on its 10 Mega byte hard disc, a continuous bar-graph Spectral Display is keeping the user in touch with the current sample being counted. This live display enables quick user interaction as well as a printout of observation for future reference.

Apart from these multiparameter MCA facilities the counter can be independently set up to register conventional cumulative counts within 8 user selected independent, consecutive or overlapping energy windows, each defined by their own Lower and Upper limit discriminators. Data printout and cumulative software supported computing enables traditional counting parameters (statistics, reproducibility and age and error computations) to take place simultaneously with the MCA based *Windowless* counting approach (Polach, Robertson, et al., 1983), supported by its PC based Windowless software. This 'W' programme enable the display of several spectra on a high resolution video terminal or plotter-printer and manipulate or massage these in the normal MCA manner. Options are: spectral stripping, summing, emphasis of region(s) of interest, integration of counts between set limits and count ratios of various regions. The 'W' software further enables automatic optimal counting window selection based on highest stability consistent with lowest error of C-14 countrate determination, hence best RC age and error.

The ultra low background characteristics are achieved by locating the sample within an asymmetric graded shield affording best passive attenuation of incident and self-induced interfering radiations for a shield of a given mass. The sample and the phototubes are also surrounded by an asymmetric active liquid scintillation guard which further and significantly reduces the residual background. This combination can be enhanced by placing an optional external gas-proportional multi-wire flat guard on top of the shield. The electronics include an independent high voltage supply and an anti-coincidence pulse gate for this purpose.

The long term stability (years) and noise free operation required of a low-level counting system are achieved by *Electronic Optimisation* (Polach, Nurmi, et al., 1983) which includes (i) automatic and continuous stabilisation of PMT gain (ii) selection of coincidence bias (iii) attenuation of cross-talk between PMTs (iv) suppression of static charge, RF interference and spurious pulses and (v) noise free Peltier element temperature control (cooling and heating).

The flexibility and performance of the system are further enhanced by the use of especially developed teflon (PTFE)/copper counting vials (Polach, Gower, et al., 1983). These are available in 3, 7, 15 and 20 ml sizes all conforming to the standard 20 ml glass vial dimensional specifications (hence all are fully interchangeable).

Results and Discussions

The Quantulus prototype, the experimental model, has now been operating continuously for 1 year at Wallac Research Department and later, for 10 months, at the ANU RC Laboratory. Its performance from the start was and remains outstanding in terms of counting efficiency, stability and reproducibility, low background, MCA resolution and user friendliness.

Stability and reproducibility can only be described as meeting the most rigorous statistical requirements of random distribution of countrates. Taking *all the data* accumulated over almost 2 years, without rejection of one single pulse, we get a perfectly statistically normal distribution of countrates around their mean. Multichannel comparisons of 1024 channel master spectra of standards, backgrounds as well as of repeats of unknowns demonstrate channel by channel stability — hence statistical reproducibility not only of the sealed standards but of repeat sample preparations. These repeats include combustion and benzene syntheses as well.

Performance data are presented in Table 1. A comparison to a conventional modern

Table 1. QUANTULUS Performance, full sample size.

Vial	1) Vol ml	2) B cpm	3) E %	4) fM No/$\sqrt{(B)}$	Age limit, yrs BP counting time		Precision % M counting time	
					1K min	4K min	1K min	4K min
PTFE/Cu[+]	20	1.0	77	159	60,100	65,700	.34	.17
»	15	0.9	77	137	58,900	64,500	.4	.2
»	7	0.5	75	84	55,000	60,000	.6	.3
»	3	0.17	74	59	52,100	57,700	.9	.45
GLASS*	5	4.5	75	20	43,500	49,000	.8	.4

[+] PTFE/Cu vials in QUNTULUS (Polach, Gower, et al., 1983)
* GLASS vials, low in K-40, in conventional modern liquid scintillation counter tuned for C-14

1) Volume of sample benzene in ml = capacity of vial
2) Background (B) cpm
3) % counting efficiency
4) RC dating 'factor of Merit' (No/$\sqrt{(B)}$) where
No = .95 oxalic ref.std. countrate

— Age limit calculations are based on equal counting time of background, standard and unknown
— Precision, % Modern, is error when unknown countrate = standard countrate and includes background errors.

Table 2. QUANTULUS Performance, small samples.

Vial 3 ml	5) Wt.C mg	2) B cpm	3) E %	4) fM No/√(B)	Age limit, yrs BP counting time		Precision % M counting time	
					1K min	4K min	1K min	4K min
PTFE/Cu+	80	0.17	74	2	24,900	30,500	5.9	3.0
»	160	»	»	4	30,400	35,900	3.9	1.9
»	400	»	»	10	33,800	43,300	2.3	1.2
»	800	»	»	20	43,300	48,900	1.6	0.8
»	2400	»	»	59	52,100	57,700	0.9	0.5

5) weight of elemental carbon

counter with glass vials is also made. It is rewarding that a precision of better than 0.2 % Modern and an upper age limit of 65 Ky BP can be achieved by the Quantulus.

The merit of low backgrounds is best illustrated when small sample dating is necessary. Table 2 gives the performance of the Quantulus for small samples using the 3 ml teflon/copper vial. Even 80 mg of carbon (equivalent to ca. 0.1 ml of benzene) give a precision of 3 % M and an upper age limit of 30 Ky BP. This opens new horizons in C-14 dating by liquid scintillation spectrometry and enables high precision and resolution age determinations in an average laboratory environment.

REFERENCES

Currie, Lloyd and Polach, Henry, 1980. Exploratory Analysis of the International Radiocarbon Cross-calibration Data; Consensus Values and Interlaboratory Error. Radiocarbon 22, 933—935.

Kojola, H., Polach, H., Nurmi, J., Oikari, T. and Soini, E., 1984. High Resolution Low-level Liquid Scintillation Beta-Spectrometer. Internatl. J. Applied Radiation and Isotopes, in press.

Libby, W.F., 1946. Atmosphere Helium Three and Radiocarbon from Cosmic Radiation, Physical Review, 69, 671—672.

Mook, Willem G., 1983. International Comparison of Proportional Gas Counters for 14C Activity Measurements. Radiocarbon 25, 475—484.

Polach, H.A., 1969. Optimisation of Liquid Scintillation Radiocarbon Age Determinations and Reporting of Ages. Atomic Energy in Australia, 12, 21—28.

Polach, Henry A., 1972. Cross Checking of NBS Oxalic Acid and Secondary Laboratory Radiocarbon Dating Standards. In 8th International Conference on Radiocarbon Dating, Lower Hutt, New Zealand, 2, 688—717.

Polach, H., 1974. Application of Liquid Scintillation Spectrometers to Radiocarbon Dating. In Liquid Scintillation Counting: Recent Developments, Ed. P.E. Stanley and B.A. Scoggins, Academic Press, N.Y., p. 153—171.

Polach, Henry A., 1975. Radiocarbon Dating as a Research Tool in Archaeology: hopes and limitations. In Symposium on Scientific Methods of Research, ed. Noel Barnard, National Gallery of Victoria, Melbourne, Australia, p. 255—298.

Polach, Henry, Gower, John, Kojola, Hannu and Heinonen, Aku, 1983. An Ideal Vial and Cocktail for Low-Level Scintillation Counting: copper-shielded PTFE (Teflon) and butyl-PBD. Advances in Scintillation Counting, Banff, University of Alberta Press, p. 508—525.

Polach, Henry, Nurmi, Jarmo, Kojola, Hannu and Soini, Erkki, 1983. Electronic Optimization of Scintillation Counters for Detection of Low-Level H-3 and C-14. Advances in Scintillation Counting, Banff, University of Alberta Press, p. 420—441.

Polach, Henry, Robertson, Steve, Butterfield, Derek, Gower, John and Soini, Erkki, 1983. The 'WINDOWLESS' Approach to Scintillation Counting: low-level C-14 as an example. Advances in Scintillation Counting, Banff, University of Alberta Press, p. 494—507.

Polach, Henry, Kojola, Hannu, Nurmi, Jarmo and Soini, Erkki, 1984. Multiparameter Liquid Scintillation Spectrometry. Nuclear Instruments and Methods 233 B5, 439—442.

Scott, E. Marian and Baxter, M.S., 1980. University of Glasgow, Scotland, personal communication.