LIQUID SCINTILLATION ^{14}C SPECTROMETRY: ERRORS AND ASSURANCES

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ABSTRACT. Liquid scintillation (LS) ^{14}C spectrometry, using ultra low-level, high-efficiency and resolution α and β particle detection equipment is seen as an excellent tool supporting future ^{14}C radiometry. Modern technology ensures electronic excellence: high-precision, small-sample (100mg) dating ability, flexibility of use for the detection of α and β particle emitting radioisotopes at and below natural abundance levels. Multiple applications to environmental research, supported by elegant software and commercial availability, are its attributes. However, mastering the new technology takes time as lessons learned in gas-proportional ^{14}C radiometry and high-background counting are not directly applicable to ultra low-level ^{14}C LS spectrometry using benzene as the counting medium. That discordant results can be obtained by any technique based on physical measurement is well established. This is demonstrated for ^{14}C age determination by reference to an international cross-check organized by the University of Glasgow. Reasons for aberrations are explored and the question is raised if it is not timely to introduce the type of quality assurance practiced by other analytical disciplines. Better results will not only serve the daters and users but will generally enhance the value of worldwide ^{14}C research.

LIQUID SCINTILLATION SPECTROMETRY

Advantages

Liquid scintillation (LS) spectrometry, rather than fixed window counting, is the key feature of modern radiometric equipment. As the concern for our environment increased, the detection of radioisotopes at environmental concentrations became an important aspect of many research activities. This prompted the development of LS spectrometers that have a very high isotope counting efficiency and spectral resolution accompanied by an ultra-low background. Modern LS spectrometers boast a ^{14}C signal (defined as 95% of the NBS oxalic reference standard count rate) to background ratio of 100–180, depending on vial size and location (Kaihola *et al*, 1988) and are able to determine, with 2.5% precision modern, samples of 100mg carbon content (Polach *et al*, 1988).

The technology involves multi-parameter multi-channel analyses and anticoincidence active shielding incorporated in a relatively massive (for LS counters) passive shield. Electronic optimization is achieved by software-variable coincidence bias or pulse amplitude comparison (PAC) and simultaneous α and β particle monitoring and software-variable pulse shape analysis (PSA) (Oikari *et al*, 1987).

A promising innovation with near-equivalent performance at greatly reduced cost is a photo-sensitive light guide/sample holder in the counting chamber and fine tuning of the PSA circuit. This gives a quasi-anticoincidence mode of operation (Noakes & Valenta, 1988).

Software features in dedicated low-level counters now include low-level statistical count-rate evaluation and validation parameters as well as ^{14}C age calculations based on "soft window" master and sample pulse height spectral analyses (Polach *et al*, 1983).

Disadvantages

Like all new techniques, LS spectrometry – inclusive of LS counting, has to be mastered. It appears to reviewers that one of the fundamental reasons for unreliable LS results is the lack of experience in this type of analysis which involves: sample preparation for counting, benzene purity, selection and usage of scintillation cocktails, selection of counting vials and their calibration, equipment setup and maintenance parameters, performance and long-term stability evaluations, and application of new statistical criteria when evaluating ultra-low-level count rates. To simply apply and translate gas-proportional experience to low-level LS spectrometry is inappropriate, inadequate, and leads to gross errors (Otlet & Polach, in press). To simply apply high background count rate (>2cpm) statistical evaluations to ultra-low-level count rates (<0.3cpm) is equally inappropriate (Currie, 1988; Currie & Parr, 1988; Polach, 1987).

VARIATION IN COUNT RATES AND PERFORMANCE

Haas (1979), Pearson (1979) and Gupta and Polach (1985) give detailed descriptions of LS counting procedures. Enhancements of ^{14}C validation, such as radon monitoring, are described by Polach and Kaihola (1988) and radon elimination by Hood *et al* (1989). Factors causing variation in count rates and performance by LS radiometry include: benzene contamination and/or quenching, photo- or chemi-luminescence, tritium (^{3}H), radon (^{222}Rn), foreign sources of ^{12}C, ^{13}C or ^{14}C, memory effects, benzene synthesis apparatus or counting vial or cap contamination, variation in count rate of ^{14}C-labeled and ^{14}C-free standards, C_6H_6 synthesis catalyst, isotopic fractionation during benzene synthesis, variation of ^{14}C detection efficiency and background count rate, equipment problems or failure and cosmic and other radiations or external interference.

A major factor affecting the global validity of ^{14}C results remains the determination of the activity of the ^{14}C dating reference standards used. The notion that we must prepare for counting the sample and standard, and determine the ^{14}C activity, in exactly the same manner is correct. However, this is not always a simple matter! We know, for example, that isotopic fractionation of all standards can and will occur, due to their chemistry (eg, Polach & Krueger, 1972) or during CO_2 purification and benzene synthesis. We know also that it is not sufficient to determine this fractionation mass spectrometrically as there are situations when the δ^{13}C correction is ineffective (Polach, 1972). Past international standards calibration studies showed that outliers did occur. Some disagreement, outside statistics, is therefore to be expected when comparing data from many sources.

INTERLABORATORY TEST

Reference standard calibrations are a form of interlaboratory cross-checks. Even though the participants of past calibration runs were selected from amongst the best known research laboratories some outliers appeared. However, grouping of the results enabled a statistically valid calibration of internationally accepted ^{14}C dating standards.

Blind dating of the same material by non-selected laboratories, on the other hand, may yield widely divergent results. Here are presented results of one of the pure-labeled benzene sample pairs of identical ^{14}C activity the ^{14}C age determinations of which were carried out by 18 anonymous LS laboratories as a blind test (Table 1).

TABLE 1

Liquid scintillation intercomparison. Results are based on *identical benzene* sample pairs counted by anonymous participants (Scott *et al*, in press)*

Lab	Result	Error	Lab	Result	Error	Lab	Result	Error
a	490	60	g	740	55	m	1010	40
	710	65		850	55		1020	40
b	540	140	h	743	39	n	1070	40
	660	145		882	39		1070	40
c	560	50	i	800	40	o	1228	46
	650	50		910	45		1382	48
d	688	34	j	860	25	p	1195	35
	703	32		870	25		1375	35
e	680	170	k	870	40	q	1387	1000
	730	140		940	45		1585	640
f	570	90	l	940	50	r	1603	46
	980	100		1020	50		1672	69

* The 36 results were ordered in increasing ages of identical sample pairs. Alphabetic codes bear no relationship to those used in the quoted reference.

The results are ordered in ascending age of sample pairs and the laboratories are listed alphabetically. Table 1 and Figure 1A show the results to range from 490±60 to 1670±70 BP. The histogram of the central values, irrespective of their errors, indicates no satisfactory grouping (Fig 1B). Hence, based on this study alone no decision can be made which, if any, are correct. To do this, additional tests needed to be and were carried out outside the framework of the Glasgow study. These tests involved the cross-checking of results necessary for tree-ring calibration studies (Stuiver, Mook & Münnich, pers commun, 1988). The tests indicate, to my satisfaction, that the correct age is 700 BP (dotted line in Fig 1A and arrow in Fig 1B). The lesson to be learned from this is age old:

Chemical and physical measurements are subject to determination errors which, if all parameters have been attended to correctly, group themselves statistically around a mean value with few outliers. If, on the other hand, something went drastically wrong, as for example with the above determinations, then we are faced with a situation when no statistics apply and interpretation is impossible without invoking additional knowledge. Measures facilitating the corrections of deficiencies suggest themselves as being timely and appropriate.
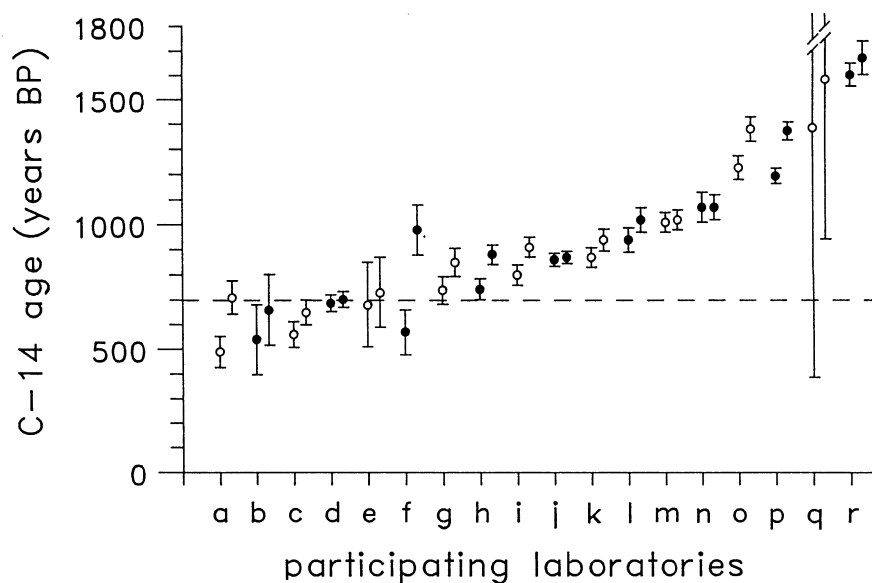
Fig 1A. Benzene, identical sample pairs, dated by 18 anonymous participants (Scott *et al*, in press). The 36 results were ordered in ascending age of sample pairs and the laboratories are listed alphabetically. Alphabetic codes bear no relationship to those used in the quoted reference. Reported ^{14}C ages range from 490±60 to 1670±70.
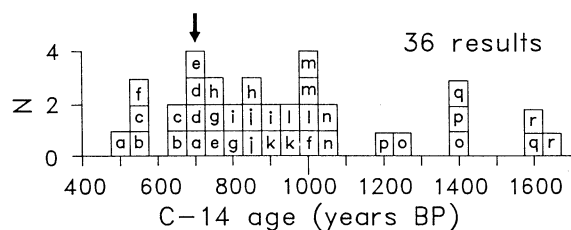

Fig 1B. Histogramatic representation of the central age values (Table 1), irrespective of their errors, indicates no satisfactory grouping. Alphabetic codes are identical to those used in fig 1A. Concensus alone cannot establish the correct age. The correct age assessment, dotted line in fig 1A and arrow, this fig, is based on additional tests carried out outside the framework of the Glasgow study given in the reference.

    The situation is not confined to LS counting. It is my view that gas proportional and mass spectrometric (^{13}C and ^{14}C) intercomparisons did not produce better results. If nothing else, alignment problems do exist for some, and at worst, proper experimental, data validation and calibration procedures were not observed by others.

    In an ideal world, appropriate scientific training allied with an attitude of individual responsibility should suffice to achieve and maintain global validity of ^{14}C determinations. Peer and user acceptance of the overall quality

of scientific ^{14}C output is high. Nevertheless, we must recognize that there are some definitive problems in this area. How this situation could be elegantly rectified remains an open question. Many ^{14}C dating laboratories provide proof of the quality of their own determinations, such as is the standard case with other analytical disciplines. Perhaps a way can be found for all dating laboratories to follow suit?

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