APPLICATIONS OF LOW LEVEL LIQUID SCINTILLATION COUNTING

J.E. Noakes
Center for Applied Isotope Studies
University of Georgia
Athens, Georgia, U.S.A.

ABSTRACT

Low level liquid scintillation counting is reviewed in terms of its present use and capabilities for measuring low activity samples. New areas of application of the method are discussed with special interest directed to the food industry and environmental monitoring. Advantages offered in the use of a low background liquid scintillation counter for the nuclear power industry and nuclear navy are discussed. Attention is drawn to the need for commercial development of such instrumentation to enable wider use of the method. A user clientele is suggested as is the required technology to create such a counter.

INTRODUCTION

Since the conception of liquid scintillation (LS) counting some thirty-four years ago, the use of LS counters for low level counting has been of intense interest to a few, and a mild wonder for many. In the 1975 Bath, England, Liquid Scintillation Conference I was asked to give a plenary address dealing with low level LS counting. In preparing for the presentation, the literature was scanned from the early 1950's up until 1975 and a report compiled covering a comprehensive review of all reported aspects of reduced background and increased stability of LS counters[1].

Upon being asked to give a similar type presentation at this conference, a computer search was initiated covering literature from 1975 to the present for any new published work on the subject. In doing this initial search, key words such as "liquid scintillation counting", brought in over 300 references. Adding more restrictive modifiers as "low level counting", "coincidence counting", "massive shielding", and every aspect that had been dealt with in the 1975 paper, the result brought forth five articles that had been published over an eight year period[1-6]. The question which then arose was, with such apparent little interest, was it really worth presenting a paper on this topic? A perhaps more important question was, did this small number of publications reflect current activities being carried out in the field of low level LS counting?

The first question is answered in that this paper deals not with improved technology related to low level counting, but to its application. The second question, that of current use, appeared the obvious topic to pursue since our laboratory is routinely doing low level counting on a daily basis with an ever increasing tempo and diversity of uses, and this information should be of benefit to the LS counter user.

In the past, when I have had occasion to present papers on various aspects of low level counting there has been two goals in mind. First and foremost has been the desire to disseminate information which would assist the low level counting community in more precise measurement of their low activity samples. The second goal, and one that I am sure has been jointly shared with my fellow colleagues in low level LS counting, has been the hope that the information presented would somehow spark the interest of the manufacturers of LS counters, thus resulting in a commercial counter being developed with low level counting capabilities. The fact that over the years we have failed to distract them from their continuing endeavour for better quench correction, faster data handling, greater sample capability, and increased automation, can only be seen as proof that we have failed to get our message across. It is, therefore, one of the goals of this paper to not only inform the user of the various applications of low level LS counting, but to take a new tack and attempt to show the instrument makers that, indeed, there is a clientele out there who would like to see a low level capability incorporated into a commercial counter and that the numbers are significant enough to warrant their attention.

Before purusing the various applications of low level counting, it might we well to define when a user enters the realm of low level counting. This can best be answered by stating that when one attempts to measure sample activities which approach the background of the counter, he had joined the esteemed ranks and acquired all the problems of low level LS counting. At this point, it might also be appropriate to state that one should not pursue this endeavour unless one has time for long counting periods, is patient in nature, and perhaps most of all, is willing to put strong faith in the statistical approach which is needed to deal with the data handling.

RADIOCARBON

Perhaps the ultimate in low level radiocarbon measurement is that activity which is called radiocarbon dating. In this procedure, the ^{14}C specific activity of known age, pre-bomb carbon samples are measured against samples of unknown age. Using the known decay rate of ^{14}C, one can estimate the date at which the sample material was taken out of exchange equilibrium with the atmosphere. In plant tissue this would correspond to the duration of photosynthesis. In the animal kingdom it would relate to the living time span of the organism. The maximum ^{14}C activity measured is pre-bomb 1950 referenced material having a specific activity of approximately 14.27 disintegrations per minute per gram of carbon (dpm/g C). With a balanced point setting for the LS counter and lower discriminator set above the E_{max} for tritium counting, one can expect a counting efficiency of near 75 percent. This, then, puts expected modern count rate at near 10.5 counts per minute per gram of carbon (cpm/g C). As most commercial LS counters have a ^{14}C background of near 20 counts per minute this leaves a 0.5 signal/noise ratio to deal with in the highest activity samples. Since most dates (approximately 80 percent at the University of Georgia Laboratory) fall in the 10,000 years before present (B.P.) data range, this means a two half-life decay has reduced the ^{14}C activity for this age range to near 2.5 cpm.g C. With smaller amounts of sample than one gram of carbon, which is usually the case, the specific activity will be proportionally less.

I mention this method only as a means to demonstrate what low levels of ^{14}C can be measured with surprising accuracy. Also, I would like to point out to the LS manufacturers that there are approximately 105 radiocarbon dating laboratories in operation today, over half of which use the benzene LS counting method for dating[7]. If these labs are similar to ours, which has six LS counters, old and updated as necessary with new electronics, this would represent a potential market of near 300 LS counter sales. The desire for purchasing new instrumentation would be greatly increased if the counters were uniquely suited to low level counting.

A second area of interest for low level ^{14}C counting has recently arisen with the food industry. Adulteration of food materials with additives other than those originating from the natural origin has become commonplace. This is due in part to the strong desire on the part of the consumer to always purchase a uniform product. Natural products can vary wildly in content due to factors such as variation in harvest time, rain fall, etc., and to remedy these discrepancies, food producers are forced to use additives. A second factor is that some adulterations are motivated perhaps more from a profit motive than for a desire to please the public's whims. In either case, the usual ingredients used are additives of low cost and are most often synthesized from petroleum derivatives which, because of their age, are devoid of any ^{14}C. Examples of just a few of these synthetic additives which find their way into food stuffs are caffeine, acetic acid, vanallin, cinnamic aldehyde, piperine, estragol, anethol, peppermint, spearmint, and the list goes on. Since the chemical composition of synthetic additives are identical to that of their natural counterparts, normal chemical analyses reveal no differences. Radiometric determination of the synthetic food additives does not present as difficult a measurement as that described for radiocarbon dating, although the comparison to a modern natural standard and the needed countng statistics are very similar. Modern ^{14}C count rate of plant material grown today is approximately 18 dpm/g C, which is 25 percent higher than a 1950 standard reference material, due to the ^{14}C bomb fallout contribution. Any decrease in the 18 dpm/g C specific activity signals the presence of a synthetic additive and the percent decrease indicates the amount of adulterant added. Using this procedure it is possible to detect as little as 3 percent adulteration in many food stuffs at a 95 percent confidence level[8].

Another example of food stuff adulteration is that which occurs in alcoholic beverages. Synthetic alcohol finds its way into a variety of alcoholic beverages by being sold to the unsuspecting beverage manufacturers as grain alcohol. This same product is also of concern to the federal government which monitors whether a grain or synthetic alcohol is used in gasahol. The importance to identify the source lies in the fact that the synthetic alcohol is not from a renewable source and therefore does not qualify for a gasoline tax reduction. Probably one of the most interesting synthetic additives to alcoholic beverages is carbon dioxide gas. If a champagne states on the label that it is fermented in the bottle, then by federal law, all the CO_2 gas dissolved in the champagne must be of natural origin. This is not always the case and when some fermentation processes fail to generate the desired "pop and fizz" when opening the bottle, the winery is inclined to add their own CO_2 source. If, as has been the practice in the past, the CO_2 is derived from carbonate rock which contains no ^{14}C, this additive can easily be identified by sampling and measurement of the $^{14}CO_2$ dissolved gas in the drink. These analyses are relatively easy to carry out but one finds difficulty in discarding the unused drink down the drain. All of the above mentioned ^{14}C food stuff analyses, and most likely many more not disclosed, are being pursued with vigor by the food industry and the federal government. It would be difficult to estimate the clientele which could use a low level LS counter for this application but to date our laboratory has received over 20 inquiries of this nature from the food industry and federal laboratories.

The industrial community is also starting to take interest in low level radiocarbon measurements. The radiocarbon isotope has always been used extensively in various industrial research efforts. However, recently, with the new federal regulations on radioactive and toxic chemical waste disposal, an effort is being made, from cost as well as health considerations, to reduce the level of generation of this material. E.I. Du Pont de Nemours & Company has for several years utilized our low level counting facilities to assist them in carrying out research and product development using ambient and sub-ambient levels of radiocarbon tracers. A few of the advantages they cite for using low levels of radioactive tracers are that once their studies are completed they can readily utilize the finished materials in other studies with little worry of radiation considerations and can readily dispose of the finished products by conventional disposal procedures. Our laboratory participation in their research programs stems only from our low level counting capability. It is not that Du Pont's research facility lacks ample available LS counters, but that their commercial instruments are not suited to this application. To estimate the industrial clientele that could utilize such counters is difficult at present but as the waste disposal problem increases the interest could pick up considerably.

The nuclear power industry is also a generator of ^{14}C. The two types of power reactors in use today are the pressure water reactors (PWR) and the boiling water reactors (BWR), each of which produce and release in gaseous form an estimated 8 to 9.5 curies (Ci) per year when operating at a power output of 3400 million total watts per year [3400 MW(t)/yr][9]. This ^{14}C production is not considered to be significant by the Nuclear Regulatory Commission (NRC) and does not require its routine measurement. However, if one considers that there are 82 such facilities operational in the United States and another 56 in various stages of construction, the total ^{14}C output could approach between 656 to 780 curies per year at present and 1100 to 1300 curies per year in the near future. ^{14}C measurements of environmental samples obtained from areas around operating reactors are being evaluated and if activity levels should increase with time, each reactor site could utilize a LS counter of low level capability to measure the slight incremental increases. The difficulty of this measurement could be considerable unless a counter could be designed so as to not only measure low activity samples but to also function in an elevated radiation background in some cases.

Hospitals, universities and colleges have always been prime users of radiocarbon both in research and routine analytical procedures. To make an estimate on what impact the use of low level counting could have to these institutions can only be speculative. However, the problems stated for industrial waste dispoal can also be applied here. Since the amount of radioactive waste which is allowed to be held or stored depends on its radioactive content, reduced costs of disposal could be achieved with lower levels of ^{14}C application. The days of "add a little more to make up for the poor counting efficiency" or to reduce the count time may be coming to a close.

TRITIUM

In the past, low level tritium (^3H) counting has been predominately associated with tracer studies dealing with ground water movement, upper atmospheric circulation and wine dating. Recently considerably more attention is being placed on measurement of ^3H generated from nuclear power reactors. As was stated previously, there are 82 nuclear power plants operational today in the United States and another 56 to come on line. The ^3H gaseous release of a BWR at 34000 MW(t)/yr is calculated to be near 85 Ci per year and a PWR, at the same power output, close to 1360 Ci per year. It should be stressed that these values are only for gaseous releases and do not include the levels contained in the coolant waters which could be considerably higher. If we apply the figure of 82 current operational nuclear power facilities to the release levels for both kinds of facilities we come up with a ^3H release figure of between 6.97×10^3 to 1.12×10^5 Ci per year at present and could rise to between 1.17×10^4 to 1.88×10^5 in the future. Unlike the ^{14}C reactor production, this level of generation is considered to be of significance to the NRC and there are mandatory requirements for reactor personnel and environmental considerations. In routine bioassay measurements of urine, a minimum detectable concentration (MDC) of 0.01 to 0.02 micro curies per liter (μCi/l) is required. Using a commercial LS counter with a ^3H background of 20 cpm, a 0.5 ml urine sample and an aqueous cocktail giving a counting efficiency of 17 percent, this level of detection can be achieved within a five minute count time. This duration of counting would not appear to be excessive, but if one considers that most counters in a power reactor facility operate at elevated background levels, this time can be greatly extended. The same analogy can be extended to environmental samples where ^3H levels are usually considerably reduced. At this lower level, it may not be possible to obtain valid data at these facilities for any extended counting time. Where the need for low level counting of ^{14}C from power reactors was projected as plausible, the ^3H low level counting application is very much more reasonable. While it is evident that a lot of "ifs" have been used for the above statements, the real facts are that our laboratory, and I would suspect many others, do a considerable number of ^{3}H measurements for power reactor facilities which have commercial LS counters but find problems with their application as stated above.

A nuclear navy is also an area where low level background counting for ^{3}H could find application. For the same reasons cited above for power reactors, ^{3}H levels for personnel aboard nuclear powered vessels must also be routinely monitored. It would be most difficult to estimate the ^{3}H production from such power facilities as this information is no doubt classified; however, one can speculate that a nuclear submarine which operates with a reduced size reactor but with recirculated air would most certainly require most personnel to be frequently monitored for ^{3}H in urine. This could entail considerable analyses per day per vessel. One could argue that the ^{3}H background levels of an LS counter, submerged underwater, would have reduced cosmic radiation because of the water shielding and, therefore, give better background performance. However, a recent report proposing disposal of decommissioned nuclear submarines in the ocean depths, discloses that after defueling each vessel will contain a projected residual radioactive level of 62,000 Ci[10]. It would seem safe to say that this radiation effect should offset any water shielding and raise the background levels of an LS counter. To estimate the nuclear navy needs for such a low level counter one can take from the same report a projected need to dispose of 120 nuclear submarines in the next 20 years[10]. From these figures, it may be assumed this is a reasonable lower level to be operational today. Add to this estimate a nuclear surface fleet of perhaps half this number and the total needs are near 180 vessels which could benefit from the use of a low level LS counter. These calculations are only taking into account estimated U.S. Navy needs and not those of our Nato Allies. Certainly with our current desire for strengthening our nuclear defense capabilities this number will go higher.

Industry, hospitals, universities and colleges, and government laboratories all utilize ^{3}H for research and routine radiometric analyses. To estimate how and to what levels this radioisotope is utilized for low level counting would only be speculative since current literature searches reveal little acknowledgement of this fact. It is safe to say that the same analogy made for the ^{14}C LS waste can be applied to the ^{3}H as well. Surely the 500,000 liter level of radioactive LS waste generated each year in the U.S. could be sizeably reduced in radioactivity if the philosophy, capabilities, and use of low level LS counting were better understood and practiced[11].

OTHER RADIOISOTOPES

Radiocarbon and tritium are by far the most frequently used radioisotopes for LS counting both in the conventional and low level mode of counting. There are, however, several other radioisotopes which are cited here as an example which have been, or could find advantage by being, measured with a modified low background LS counter.

The measurement of alpha emitters by LS counters was first reported in the literature as early as 1964[12]. Apparently, the advantage of near 100 percent counting efficiency was offset by poor energy resolution and high background which greatly restricted the routine use of the method. Recently, new interest has been directed to this means for measuring environmental levels of ^{232}Th, ^{228}Th, ^{224}Ra, ^{239}Pu, and ^{216}Po. To eliminate the drawbacks of poor energy resolution and high background, a modified LS counter-pulse shape instrument has been developed which is capable of 200 to 300 KeV energy resolution and backgrounds of 0.01 cpm[13,14].

Radioiodine (^{125}I and ^{131}I) have found extensive use in the medical field for radioimmunoassay and to a lesser extent in environmental monitoring. The choice of measurement for most of the medical applications is gamma spectroscope using a NaI(Tl) detector and pulse height analysis. Recently LS counting has also been applied to biomedical samples of relatively high activity where background considerations do not compromise the sensitivity of the method or extended counting time[15]. Environmental samples do require the use of low background instrumentation to achieve the required sensitivity. In order to accomplish this goal β-γ coincidence counting of solid samples with a dual NE102 plastic-NaI(Tl) crystal detector is the preferred method of measurement[16]. The NRC requirement for measurement of ^{131}I in milk, at the 0.40 pCi/1 level, is perhaps a prime example of the extremely low levels to be measured. Recently, a method of measurement of liquid samples of low ^{131}I activity using a modified LS counter with β-γ coincidence counting capabilities has enabled environmental level samples to be counted[17]. Our lab is currently doing ^{131}I counting on milk samples at a 0.2 pCi/l level with a background of 0.001 cpm using a similar β-γ LS counting mode of measurement.

Environmental monitoring of reactor produced strontium isotopes (^{89}Sr and ^{90}Sr) are cited as two radioisotopes which could find advantage in measuring with low level LS counting. Currently these radioisotopes are measured as solid $SrCO_3$ form using a wide beta windowless proportional counter. Advantage is made of their very different decay rates and beta energy to determine the amounts of each radioisotope in the sample. Minimum required detection levels are very low, with milk and water at the 1 pCi/1 level being typical. E_{max} beta energies of the two isotopes are 1465 KeV and 546 KeV which should permit 100 percent detection by either Cerenkov or direct LS beta spectroscopy[18,19].

SUMMARY

Low level LS counting has in the past been considered to be a very restricted method for measurement of a small number of unique samples. The primary goals of this paper have been to present a cursory survey of some of the new areas of interest such as environmental monitoring, food adulteration, and bioassay where this method of LS use has found application. It is hoped that in calling attention to the versatility of the method and understanding its unique capabilities, that it may acquire better acceptance and use in the LS community.

A secondary goal of this paper has been to call attention to the need for developing low level counting capabilities into commercial counters. It is evident that not every LS user, desiring to apply low level counting procedures, is capable or willing to take the time to tune or revamp his instrument to the necessary specifications. It is only through the availability of such an LS counter on the commercial

market that this method of counting will find its full potential use. In the past, new developments in commercial LS counters have been almost solely dedicated to the needs of the medical community. It is perhaps time to draw attention away from the desire for ever better quench correction, full automation and greater sample capacity and to devote a little effort to enable measurement of small activity samples at higher sensitivity levels.

Problems with disposal of radioactive LS waste span the use of this instrumentation for all types of samples and may be the one factor which will press home the need for measurement and use of lower levels of radioactivity. This failing, an attempt has been made to delineate possible clientele who could find use for low level counting capabilities developed into commercial LS counters. In the field of nuclear power reactor needs alone, surely the projected world wide number of over 600 units for near-term operation should spur some interest.

Development of a commercial low level LS counter should not be an insurmountable task for the LS manufacturer. The literature is full of proven innovation. Recent advances reported in such areas as micro electronics, fast coincidence timing, crosstalk discrimination, lesser pulse height and pulse shape analyses promise considerable improvements. These advances combined with present-day knowledge in the use of select low noise photomultiplier tubes, graded metal shielding, anticoincidence guard and the use of low level radioactive materials for counter fabrication should enable reaching the desired counter performance needed for low level counting. Unanticipated advantages could possible result from such an instrument being developed which would open still other user capabilities.

REFERENCES

1. J.E. Noakes, "Considerations for achieving low level radioactivity measurements with liquid scintillation counters," in "Liquid Scintillation Counting." (Vol. 4) M.A. Crook and P. Johnson (eds.). Heyden & Son, London, 189-206, 1977.
2. N.S. Huskisson and P.F.V. Ward, "The estimation of low levels of carbon-14 in biological samples by alkaline extraction and liquid scintillation counting," Int. J. Appl. Radiat. & Isot. 33(4), 241-248, 1982.

3. J.H. Thorngate and D.H. Christian, "Recent developments in the detector and electronic system used for high-resolution liquid scintillation spectroscopy of alpha particles," Health Phys. 31(6), 577, 1977.

4. T. Iwakura, Y. Kasida, Y. Imoue and N. Tokunago, "A low background liquid scintillation counter for measuring low levels of tritium," Behav. Tritium Environ. Proc. Int. Symp. 163-171, 1979.

5. U. Schotterer and H. Oeschger, "Low level liquid scintillation counting in an underground laboratory," Radiocarbon 22, 505-511, 1980.

6. T. Kuc and K. Rozanski, "A small volume teflon-copper vial for carbon-14 and low level liquid scintillation counting," Int. J. Appl. Radiat. Isot. 30, 542-545, 1979.

7. R. Kra (ed.) Radiocarbon Suppl. J., private communication 10 May 1983.

8. J.E. Noakes and P.G. Hoffman, "Determination of natural product purity by radiocarbon measurements", in "Liquid Scintillation Counting: Recent Applications and Development", (Vol. 2), C.T. Peng, D.L, Horrocks and E.L. Alpen (eds.). Academic Press, New York, 457-468, 1980.

9. J.T. Collins, M.J. Bell and M.W. Hewitt, "Radioactive waste source terms", in "Nuclear Power Waste Technology", ASME, New York, 167-200, 1978.

10. T.C. Jackson and M.J. Herz, "Draft environmental impact statement (DIES) on disposal of decommissioned, defueled nuclear submarines", Ocean Soc. Sci. Comm. Report, 1-25, March 1983.

11. R.W. Granland, "Incineration of waste liquid scintillation fluid", in "Management of Low-Level Radioactive Waste", M.W. Carter, A.A. Moghissi and B. Kahn (eds.), Pergamon Press, New York, 419-427, 1979.

12. D.L. Horrocks and M.H. Studier, "Low level plutonium-241 analyses by liquid scintillation techniques", Anal. Chem. 30, 1747-1750, 1958.

13. W.J. McDowell, "Liquid scintillation alpha counting and spectrometer and its application to bone and tissue samples" in "Liquid Scintillation Counting: Science and Technology", A.A. Noujaim, C. Ediss, L.I. Wiebe (eds.). Academic Press, New York, 17-31, 1976.

14. W.J. McDowell, "Alpha liquid scintillation counting; Past, present and future", in "Liquid Scintillation Counting: Recent Applications and Development", (Vol. 1) C.T. Peng, D.L. Horrocks, E.L. Alpen (eds.). Academic Press, New York, 315-332, 1980.

15. E.D. Bransome, Jr. and S.E. Sharpe, III, "Measurement of ^{125}I, ^{131}I and other γ-emitting nuclides by liquid scintillation counting" in "Liquid Scintillation Counting: Recent Developments", P.E. Stanley, B.A. Scoggins (eds.) Academic Press, New York, 103-112, 1974.

16. D.E. McCurdy, R.A. Mellor, R.W. Lambdin and M.E. McLain, Jr., "The use of cuprous iodide as a precipitation matrix in the radiochemical determination of ^{131}I in milk", Health Phys. 38(2), 203-213, 1980.

17. S.M. Kim, Radiation Management Corporation, private communication, Philadelphia, PA, 1981.

18. R.B. Randolph, "Determination of strontium-90 and strontium-89 by Cerenkov and liquid-scintillation counting", Int. J. Appl. Radiat. Isot. 26, 9-16, 1975.

19. B. Carmon, "The use of Cerenkov radiation for the assay of radiostrontium in aqueous solutions", Int. J. Appl. Radiat. Isot. 30, 97-100, 1979.