

## PERFORMANCE OF THE PACKARD TRI-CARB® 2770TR/SL LIQUID SCINTILLATION ANALYZER FOR <sup>14</sup>C DATING

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**ABSTRACT.** We present results that demonstrate the potential of the Packard Tri-Carb® Model 2770TR/SL for radiocarbon dating. For 2 g of sample benzene, a stable background count rate of 0.307 cpm and a stable counting efficiency of 64.78% were determined using a 13–75 keV counting window. Changes to the mathematical routines for t-SIE (quench indicating parameter) calculation and a reduction in the activity of the external standard have enabled stability of the t-SIE to be achieved, and combined with the use of a suitable balance point counting window; all of these factors give the stability of performance required for <sup>14</sup>C dating. Calculations based on the above parameters indicate that the limit of detection for 2 g samples, counted for 5000 min, is >48,900 yr BP. The great advantage of this system is that these data were acquired using inexpensive standard 7-mL low potassium borosilicate glass vials. Vial holders manufactured from BGO reduced the background to 0.15 cpm with a minimum effect on efficiency (64.46% for 13–75 keV). A similar calculation of the limit of detection gave >51,700 BP. The use of the BGO vial holders in other instruments employing time-resolved liquid scintillation counting (TR-LSC) (Models 2250CA and 2260XL) also brought about significant improvements in detection limits.

### INTRODUCTION

Prior to the mid 1980s, almost all attempts at background reduction on liquid scintillation analyzers (LSAs) were made by the instrument users, many of whom were practitioners of <sup>14</sup>C dating. In effect, the <sup>14</sup>C community led the field in low-level liquid scintillation counting (LSC) during this period. These attempts at background reduction consisted mainly of modifications to existing instrumentation and included the following: increasing the amount of passive shielding, reducing the voltage applied to the photomultiplier tubes (PMTs), masking the PMTs or the vials to minimize PMT crosstalk or using alternative low background materials for vial construction (mainly quartz or Teflon™) (Tamer 1965; Calf and Polach 1974; Noakes 1977; Haas 1979; Gupta and Polach 1985). In addition, a number of experimental devices incorporating cosmic guard detectors were fabricated (Pietig and Scharpenseel 1964; Alessio *et al.* 1976; Punning and Rajamae 1977; Iwakura *et al.* 1979; Jiang *et al.* 1983). During the mid 1980s, Wallac introduced what was effectively the first commercially manufactured low-level LSA—the Quantulus™ 1220. Originally designed for <sup>14</sup>C dating, it used several features designed to reduce background, including enhanced passive shielding and an active guard device. Shortly afterwards, the Packard Instrument Company introduced a new concept in low-level liquid scintillation analysis into their Tri-Carb® LSAs, based on a type of pulse shape/duration analysis (van Cauter 1986), rather than the more conventional methods discussed above. This concept was later named time resolved liquid scintillation counting (TR-LSC) and uses what the company has termed burst counting circuitry (BCC). The BCC makes use of differences in the after-pulse patterns which follow the prompt pulses of true  $\beta$  and background events to achieve separation (Valenta 1987). Since most background prompt pulse events are followed by a number (burst) of randomly spaced afterpulses of much smaller amplitude, whereas the prompt pulse of a true low-energy  $\beta$  event is followed by very few or none, a high degree of discrimination between the pulse types could be achieved. Originally, the BCC had a factory preset delay of 75 ns between the onset of the prompt pulse and commencement of afterpulse measurement, limiting its use for high energy  $\beta$  events and slow decay constant fluors. However, over the last few years there have been significant improvements in the flexibility and performance of these instruments through the introduction of 1) a programmable delay before burst feature that allows the delay to be matched to the energy of the event and the pulse shape characteristics of the scintillant, thereby minimizing effi-

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ciency losses, and 2) quasi-active guard detectors. These devices do not have separate PMTs, but are optically coupled to the sample PMTs, operating by enhancing the burst of afterpulses derived from background radiations as they penetrate the guard, making the background rejection more effective. The development of these instruments culminated in the introduction by Noakes and Valenta (1995) of a quasi-active guard consisting of bismuth germanate or BGO ( $\text{Bi}_4\text{Ge}_3\text{O}_{12}$ ), which has been demonstrated as having considerable potential for  $^{14}\text{C}$  dating, with performance characteristics equaling those of instruments employing active guard detectors (Cook 1995). We present the results of a study designed to 1) optimize the performance of the Packard® 2770TR/SL, 2) assess its background and efficiency stability and compare the performance to a previous generation of Packard Tri-Carb® low-level counters (Packard® 2250CA), and 3) assess the effect of using BGO vial holders on background and efficiency in the 2770 and previous TriCarb® instruments.

## METHODS

We carried out all experiments using standard 7 mL low potassium borosilicate glass vials fitted with brass caps containing silicon rubber and indium foil seals and containing 2 g benzene. The scintillation cocktail comprised *butyl*-PBD and *bis*-MSB at concentrations of 2.8 and 3.0 mg g<sup>-1</sup> benzene, respectively. We added this to each vial as a benzene solution, with the benzene being removed by freeze drying, leaving the scintillants at the bottom of the vials in a finely divided form which easily re-dissolves when the sample benzene is added.

The original prototype instrument showed excess variability in the quench indicating parameter (t-SIE); we describe the steps taken to overcome this problem and the data given here are for the first tests on the modified instrument. To study quenching and the reproducibility of the quench indicating parameter (t-SIE), we prepared 16 vials containing 2 g total sample weight, comprising mainly  $^{14}\text{C}$ -labeled benzene (3566 dpm g<sup>-1</sup>) and with an increasing weight of 2% acetone in scintillation grade benzene solution to provide us with the required variations in t-SIE. We counted each sample for 100 min and stored the spectra and then made 30 measurements of the t-SIE parameter over the course of 6 cycles (5 counts per cycle). We carried this out on both the 2770TR/SL and a model 2250CA. The latter has a fixed delay of 75 ns in the BCC; the former was set to 75 ns delay. Because the PMT gains and voltages cannot be manually adjusted, the only way in which balance point counting can be carried out is through adjusting the counting window. The lower discriminator was set at 13 keV to discriminate out 99.7% of the tritium cpm; the upper discriminator was varied between 65 and 85 keV and a series of quench curves were derived. The counting window that produced an efficiency plateau at low quenching was chosen as the optimum for balance point counting and all experiments were carried out with this window.

To study background stability in the 2770TR/SL, we prepared a single vial with 2 g scintillation grade benzene and counted it for a period of 10 d (100 cycles of 100-min counts) using the balance point counting window. A similarly prepared vial was counted in the 2250CA for 4 d (100 cycles of 50-min counts). To study stability of efficiency, unquenched  $^{14}\text{C}$ -labeled standards were cycled in a similar manner (100 cycles of 25-min counts). Using the counting efficiency and background count rate derived for the balance point counting window and the limit of detection used by Currie (1968), theoretical calculations of the achievable resolution in terms of age and error were made.

## RESULTS

For a liquid scintillation counter to be suitable for  $^{14}\text{C}$  dating, accurate quench monitoring is essential. Since BGO is a very efficient gamma detector we reduced the intensity of the external standard ( $^{133}\text{Ba}$ ) from 18 to 1  $\mu\text{Ci}$ . Although this increases the time required to measure the t-SIE, the time is

insignificant in relation to that required for suitable sample counting statistics to be obtained. In addition, we employed a proprietary gamma rejection technique, based on pulse shape analysis and TR-LSC, to eliminate the long pulses (gamma-photon derived) emanating from the BGO guard that contributed to the Compton spectrum, which is derived from the interaction of the  $^{133}\text{Ba}$  gamma photons with the vial and contents. In addition, corrections to any shift in baseline or dead time are made to insure that the subtraction is performed properly. In a non-BGO system, the beta sample spectrum (SP1) is acquired and subtracted from the acquired beta + Compton spectrum (SP2) to yield the net Compton spectrum. The t-SIE is then calculated on the net Compton spectrum. In the 2770TR/SL, SP1 and SP2 are acquired but in this instance SP2 also contains the gamma contribution detected by the BGO guard. A third empty vial spectrum (SP3) is acquired which corresponds to the gamma component from the guard. The derived Compton spectrum is then the result of the following calculation:  $\text{SP2} - (\text{SP1} + \text{SP3})$ . The t-SIE parameter is then calculated on the resultant Compton spectrum. The

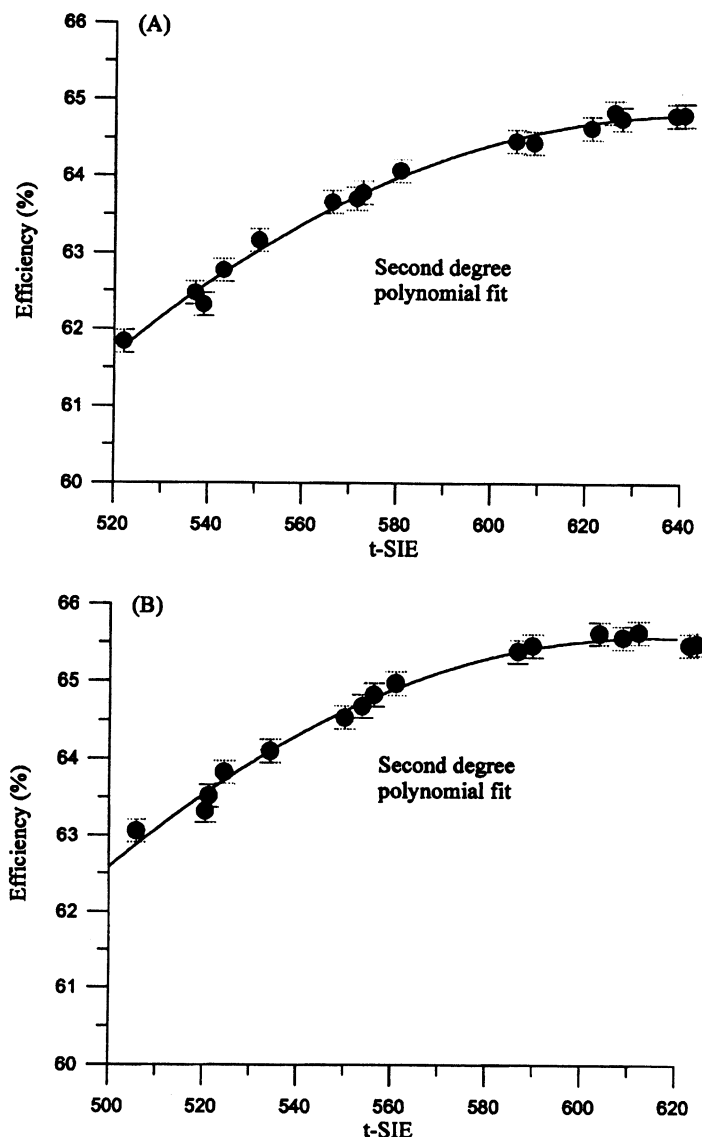


Fig. 1. Quench curves for the balance point counting window (13–75 keV) for (A) Packard® 2770TR/SL and (B) Packard® 2250CA

quench curves derived for the balance point counting window are illustrated in Figure 1. For both instruments, a counting window of 13–75 keV is approximately the optimum in terms of producing a plateau of constant efficiency. For the 2770TR/SL, we normalized the data to the least quenched standard, which had a t-SIE value of 640, and for the 2250CA to a value of 620. The quench factors and 1- $\sigma$  errors for a limited t-SIE range are given in Table 1. These demonstrate that, for both instruments, a quench factor of <1.0020 would be applied to the counting efficiency within a range of *ca.*  $\pm 20$  t-SIE units of the least quenched sample. In practice, the vast majority of benzene samples produced in the SURRC laboratory are within a total range of *ca.* 20 units and so we are effectively operating at constant efficiency, given the 1- $\sigma$  errors on the quench factors (in the range 0.0010–0.0020). We analyzed the t-SIE data for the quench curves (30 measurements per standard) and noted standard deviations of *ca.* 3 and 6 units for the 2250CA and 2770TR/SL, respectively.

TABLE 1. Quench Factors and Associated 1- $\sigma$  Errors for Samples Having t-SIE Values Around the Value for Which Data Normalization is Carried Out

2770TR/SL			2250CA		
t-SIE	Quench Factor	Error (1 $\sigma$ )	t-SIE	Quench Factor	Error (1 $\sigma$ )
660	1.0008	0.0020	640	1.0020	0.0017
655	1.0004	0.0018	635	1.0013	0.0015
650	1.0001	0.0016	630	1.0007	0.0014
645	1.0000	0.0015	625	1.0003	0.0012
640	1.0000	0.0014	620	1.0000	0.0011
635	1.0002	0.0013	615	0.9999	0.0011
630	1.0005	0.0013	610	1.0000	0.0010
625	1.0011	0.0013	605	1.0003	0.0010
620	1.0017	0.0012	600	1.0007	0.0010
615	1.0027	0.0012	595	1.0013	0.0010

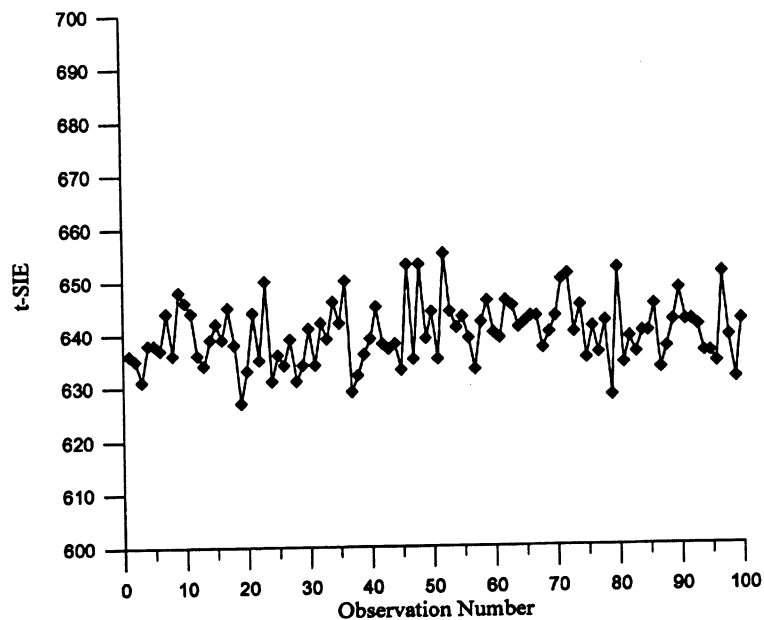


Fig. 2. t-SIE values for our least quenched standard counted in the Packard® 2770TR/SL

Figure 2 illustrates the stability of the t-SIE measurement for the 2770TR/SL. The results of the study on background count rates indicate that both instruments are stable and obey Poisson statistics. The count rate in the 2770TR/SL is reduced by about a factor of 4 compared with the 2250CA (0.307 against 1.18 cpm) (Figure 3). Similarly, efficiency measurements were also stable and obeyed Poisson statistics (Figure 4). We recounted the samples in vial holders manufactured from BGO and achieved improved performance in all cases. For the 2250CA and the 2260XL, the background count rate was reduced by a factor of *ca.* 3 and for the 2770TR/SL by a factor of 2. These data are given in Table 2 together with counting efficiencies. Figure 5 illustrates the theoretical improvement in precision that can be achieved.

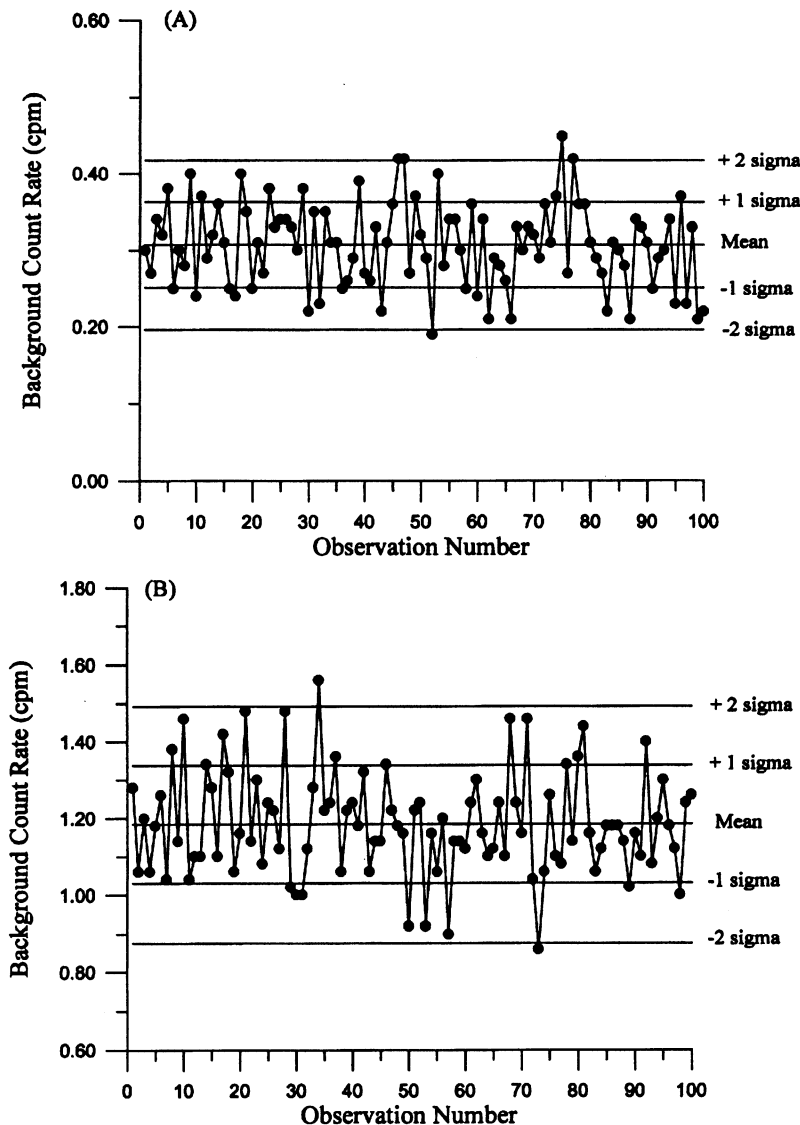


Fig. 3. Background count rate measurements for 2 g benzene in (A) Packard® 2770TR/SL and (B) Packard® 2250CA, in a 13–75 keV counting window

TABLE 2. Performance Data for Tri-Carb® Models 2250CA, 2260XL and 2770TR/SL Used With and Without BGO Vial Holders

Instrument model	BGO vial holders	% Efficiency (13–75 keV)	Background (cpm)	Minimum age
2250CA	No	64.52	1.18	>43,500
2250CA	Yes	64.83	0.34	>48,500
2260XL	No	63.03	0.54	>46,400
2260XL	Yes	63.45	0.19	>50,600
2770TR/SL	No	64.78	0.31	>48,900
2770TR/SL	Yes	64.46	0.15	>51,700

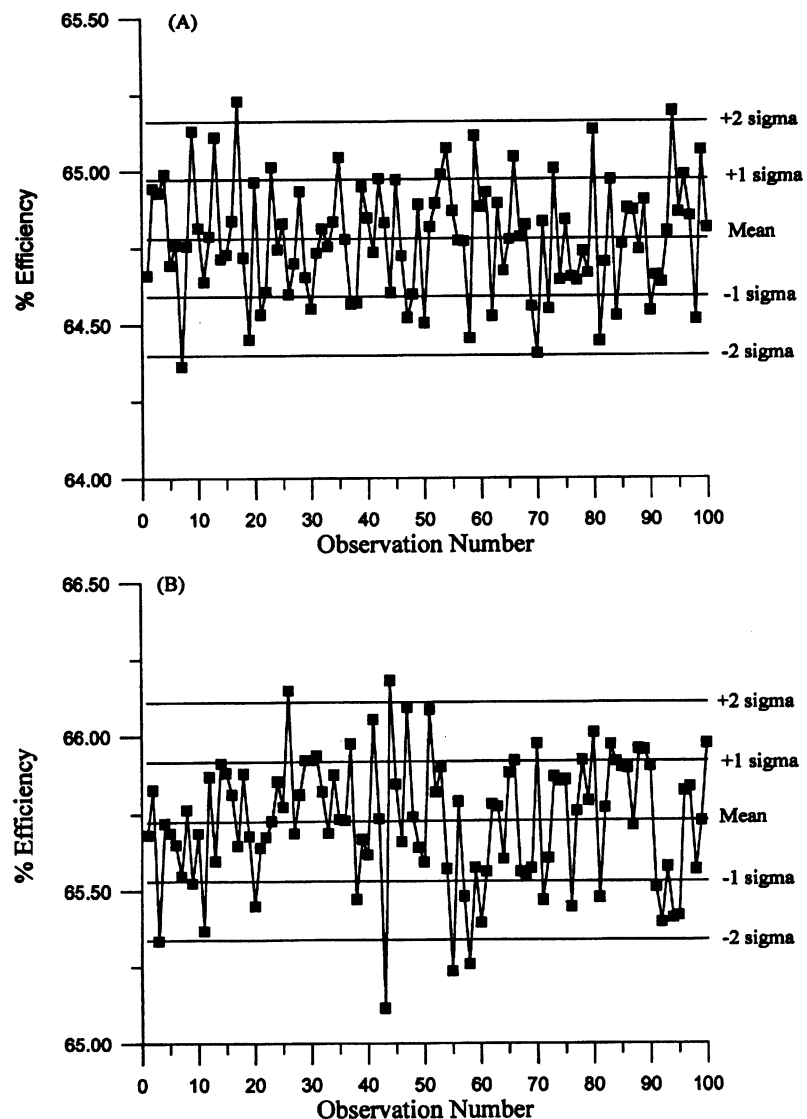


Fig. 4. Efficiency measurements for 2 g benzene in (A) Packard® 2770TR/SL and (B) Packard® 2250CA, in a 13–75 keV counting window

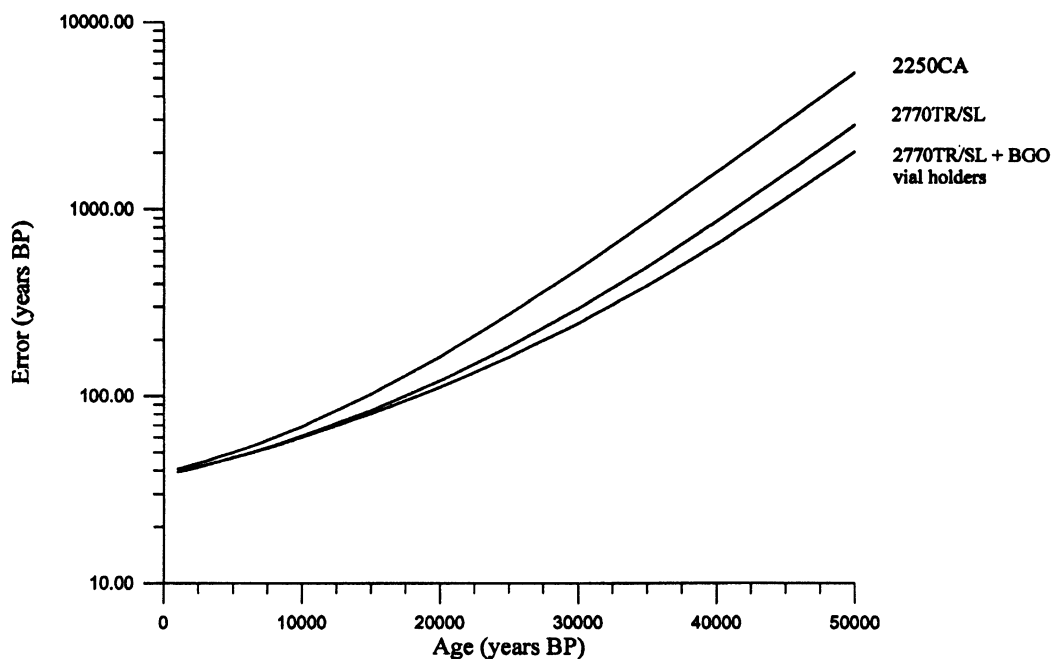


Fig. 5. Achievable resolution of the Packard® 2770TR/SL and Packard® 2250CA in terms of radiocarbon age and dating error for a sample counting time of 5000 min

## CONCLUSION

Our results show that the 2770TR/SL produces a significant improvement in performance over previous generations of Tri-Carbs. In addition, the data demonstrate that all the parameters which we measured were stable and this is of fundamental importance when considering accuracy, precision and limits of detection. This performance is obtained without the use of enhanced passive shielding, an active coincidence guard detector or special counting vials. The use of BGO vial holders brings about a further enhancement but is more limiting since only 7-mL vials or smaller can be counted using these and they are expensive to manufacture. Nevertheless, it opens up the possibility for those who operate earlier Tri-Carbs with TR-LSC to make use of this advance in technology. A single vial holder can be used with the instrument operated in a non quasi-simultaneous mode, *i.e.*, long counts (1000 min) made on single vials. This could be particularly useful for those who operate instruments such as the Model 1050, which does not have a sample changing facility in any case.

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