

## Chapter 23

# Gas-Liquid Fractional Interaction Column (Galific) as a Trapping Device in Sample Oxidizers

P. Juhala and N. Kaartinen

*Department of Physiology, University of Turku, Finland.*

When extensive sample preparation is required for liquid scintillation samples, then oxidation techniques are recommended. Oxidation eliminates most of the sensitivity-reducing factors present in other less sophisticated methods. Also LS spectrometers give their best performance with high quality samples.

Ideally any sample preparation process should not have larger variability than the measurement process (liquid scintillation counting(LSC)) itself, and preferably smaller, whereby the full potential of the LS spectrometer would be available to samples prepared with that method.

The statistical built-in accuracy of LS spectrometers is of the order of 1 in 1000, but the automatic standardization even to correct slightly quenched samples reduces the accuracy to 1 in 400. In some extensive sample preparation methods, plagued with a number of error sources, the reproducibility may drop down to 1 in 10. The potential loss of information due to poor sample preparation can be compensated for by making multiple samples as a square of the improvement required. To match the accuracy of one measurement of an LS spectrometer with automatic standardization with a sample preparation method giving 1 in 10 accuracy one requires 1600 samples of the same sample material. The lack of speed in comparison to other less sophisticated sample preparation methods has often been given as the reason for the relative unpopularity of oxidation methods.

When the present work, the improvement of oxidizer systems for tritium and carbon-14 samples, started, the main aims were set up to bring the reproducibility closer to that of LS spectrometers and with the speed to match other sample preparation methods.

So what is the performance of an LS spectrometer? None of the data published were satisfactory to us so we obtained our own.

Figure 1 shows the background stability of Packard LS spectrometer model 3375. Tritiated natural water was counted 29 times in single-count mode for 500 min over

Fig. 1. Background stability, Mod 3375

HTO-MP 40  $\mu$ l ml 5% H<sub>2</sub>O  
500 min, 24 counts single-count mode,  
3 weeks,  
MEAN<sub>c.p.m.</sub> = 17 780  $\pm$  0.217 (obs)  
MEAN<sub>theor.</sub> = 0.189 c.p.m.  
 $\therefore$  3/4 variance = Poisson v.

Fig. 2. Reproducibility of repeat count mode

$3.5 \times 10^8$  c.p.m. collected in 20 h,  
close to full scalars, stopped by  
time.  
SD<sub>theor.</sub> = 0.1165%  
SD<sub>obs.</sub> = 0.1162%  $\pm$  0.0194%

Fig. 3. Counting stability, Mod 3375

Packard standards,  $^3\text{H}$ ,  $^{14}\text{C}$ ,  
 preset windows, full scaler statistics,  
 26 counts, 3 weeks, single mode,

S.D. $^{14}\text{C}$	= 0.122% (obs)	} instrument instability less than 0.05%
S.D. theor.	= 0.105%	
S.D. $^3\text{H}$	= 0.134% (obs)	
S.D. theor.	= 0.110%	

Fig. 4. Volume independence of automatic standardization, ratio mode, Mod 3375

HTO, Monophase 40, 10%  $\text{H}_2\text{O}$  conc.

10-14 ml: 0.05% CV  
 6-15 ml: 0.5% CV

Statistics: each ml 10 times full scalers,  
 means used for statistics to reduce  
 non-relevant sources of variance

3 weeks. Mean c.p.m. was less than 18 c.p.m. and observed SD was approximately 0.2 c.p.m. and the order of instrument instability in the order of 0.1 c.p.m. Figure 2 shows the reproducibility of the repeat count mode for tritium which has been calculated with a mean count of 736 800 c.p.m. collected without changing the counting geometry; which happens, for example, when the vial is changed. The theoretical standard deviation should thus be 0.116 5% and the observed was 0.116 2, with standard deviation of 0.019 4.

Counting stability of our 3375 is shown in Fig. 3. The wide carbon window stops counting at 900 000 thus giving a theoretical SD of 0.105% and the narrower tritium window thus collects less counts giving a slightly smaller theoretical standard deviation of 0.110%. When these standards were counted 26 times in a period of approximately 3 weeks, in single mode, the difference between theoretical and observed standard deviation resulted in an equivalent of 0.07% CV from non-counting sources of variability. What is the error on the clock when the scalers are filled? From my approximate calculations the error could be in the order of 300 ms for carbon, and for tritium about twice that.

In Fig. 4, volume independence of standardization for tritium is shown using HTO 10% water concentration in monophase 40. For best precision one should stay within 10-14 ml whereby the measured 0.05% CV is negligible. For cost cutting or for large samples one has a range from 6 to 15 ml with a satisfactory 0.5% CV. For carbon these errors are considerably smaller. So it appears that the 3-4 years old Packard LS spectrometer model 3375 is working the way its designers meant it because its precision is limited mainly by the capacity of its scalers.

Returning to the question of oxidizer performance, what one needs is the filling of the many orders of magnitude between the gas bubbler and the gas chromatograph, in other words a macro gas chromatograph column with a quickly removable and replaceable liquid phase.

One candidate to fill that gap has been developed during this work. It is a narrow bore tubular column with outer dimensions similar to packed gas chromatography columns which can be folded to conserve space. It is called a gas-liquid fractional interaction column (GALIFIC). With a given maximum gas flow it traps and, through its internal geometry, holds a fixed amount of liquid which in small successive liquid fractions interacts with the gas phase flowing through, absorbs a gaseous component through chemical reaction and traps a vapour by balancing it with the vapour of the liquid or replaces a dissolved gas with another gas.

A regular column used in the Packard Model 306 Sample Oxidizer is stainless steel with a neck diameter of 2.8 mm and water holding capacity of 300  $\mu\text{l}/90$  cm. The radioactivity that passes through such a column is 3 orders of magnitude lower than the input to the column at a flow rate of 7000 ml  $\text{min}^{-1}$  in one minute at 1.2 bar.

The effect of the GALIFIC on oxidizer design is that it allows any recovery, any separation of HTO and  $^{14}\text{CO}_2$  and oxidation speed of in theory 10-20 l  $\text{min}^{-1}$  oxygen equivalent, limited by the loss of vaporization of reagents and by the necessity of accommodating the extra liquids to recover the trapped oxides. Fortunately in LSC extra liquids, the scintillator liquids, are available and form a necessary part

Fig. 5. Reproducibility of HTO system.  
1, number of sample (<sup>3</sup>H palmitic acid);  
2, mg/sample; 3, d.p.m./mg; 4, memory.  
Spill-over not detectable due to low  
counts. Recovery = 99.6%.

1	2	3	4
1.	212,86	1698,10	5,7 -5
2.	140,57	1699,70	1,6 -4
3.	179,92	1698,42	9,1 -5
4.	196,87	1698,14	8,6 -5
5.	155,38	1694,85	1,16-4
6.	198,47	1704,92	9,5 -5
7.	196,88	1700,26	1,4 -4
8.	187,49	1701,39	9,7 -5
9.	147,34	1700,14	1,0 -4
			1,09-4
		$\bar{x} = 1699.55$	
		$\pm 0.162\%$	

Fig. 6. <sup>14</sup>C performance. 1, number of sample; 2, mg <sup>14</sup>C-palmitic acid combusted;  
3, combusted d.p.m./mg; 4, memory; 5, spill-over; 6, mg standard; 7, d.p.m./mg  
standard. Recovery = 99.31%. Difference from variance combusted-standard = 0.10% CV  
for carbon process.

1	2	3	4	5	6	7
1.	114,66	2745,42	2,12-5	-1,60-6	166,19	2759,17
2.	138,46	2742,98	-2,98-5	2,12-5	154,61	2760,79
3.	119,37	2741,92	7,78-5	1,75-5	130,57	2753,11
4.	121,56	2728,43	6,12-5	1,43-5	101,00	2764,97
5.	139,30	2737,73	3,01-5	1,70-5	100,05	2754,96
6.	133,05	2740,93	5,79-5	3,33-5	145,50	2758,96
7.	144,87	2745,98	4,65-5	4,05-5	137,21	2754,77
8.	133,06	2742,43	1,83-5	-5,65-6	111,48	2762,26
9.	115,08	2750,95	3,93-5	9,49-6	114,11	2770,31
10.	158,79	2736,53	5,14-5	6,25-5	103,82	2765,62
		$\bar{x} = 2741.33$	$\bar{x} = 3.7-5$	$\bar{x} = 2.1-5$		$\bar{x} = 2760.46$
		$+ 6.13$				$+ 5.46$
		$=0.224\%$				$= 0.198\%$

of the final sample and can be used to wash HTO and CO<sub>2</sub>-carbamate to the counting vials.

So, what is the performance of Galific in an oxidizer system? We took a Packard Model 306 oxidizer and equipped it with an after burner of our own design. We burned labelled palmitic acid and the results were as shown in Fig. 5.

The first column is the number of the sample. One of the ten samples was some 5 to 6 SD away from the rest and so we have only included 9 samples. Column two is the mass of the sample in mg; column three is specific activity. Memory value is given after blasting with pressurized air manually because otherwise most of the remaining memory is retained on the vial seal.

When Tarkkanen and associates made Monophase 40, it was required to be as good for counting distilled water as homogenous counting and this slide proves that it is. The problem with these troublesome emulsion systems like MP-40 was that I was using fatty acid which is on the wrong side of the phases.

Standards gave at least twice as large a variation as our combusted samples. So we settled down to determine only the specific activity which gave 99.6% recovery.

So the tritium system works as was intended because the difference in variances between combustion and control is only 0.10% which is the normal precision from statistical-

theoretical of the Packard LSC counter we have. On the other side we believed we had very good analytical balance, but now we know better. It is only good. Some of the variability in standard values is coming from our balance, some from our 3375. Results for carbon-14 are shown in Fig. 6.

The other performance parameters beside reproducibility, the memory and spill over parameters are one order of magnitude better than the specifications of the Packard sample oxidizer, whose specifications are arbitrarily set to make allowances required by manufacturers and users' slight imprecisions.