APPLICATION NOTE

Measurement of biofuels with the Tri-Carb 4910 and comparison with the Quantulus GCT.

Author

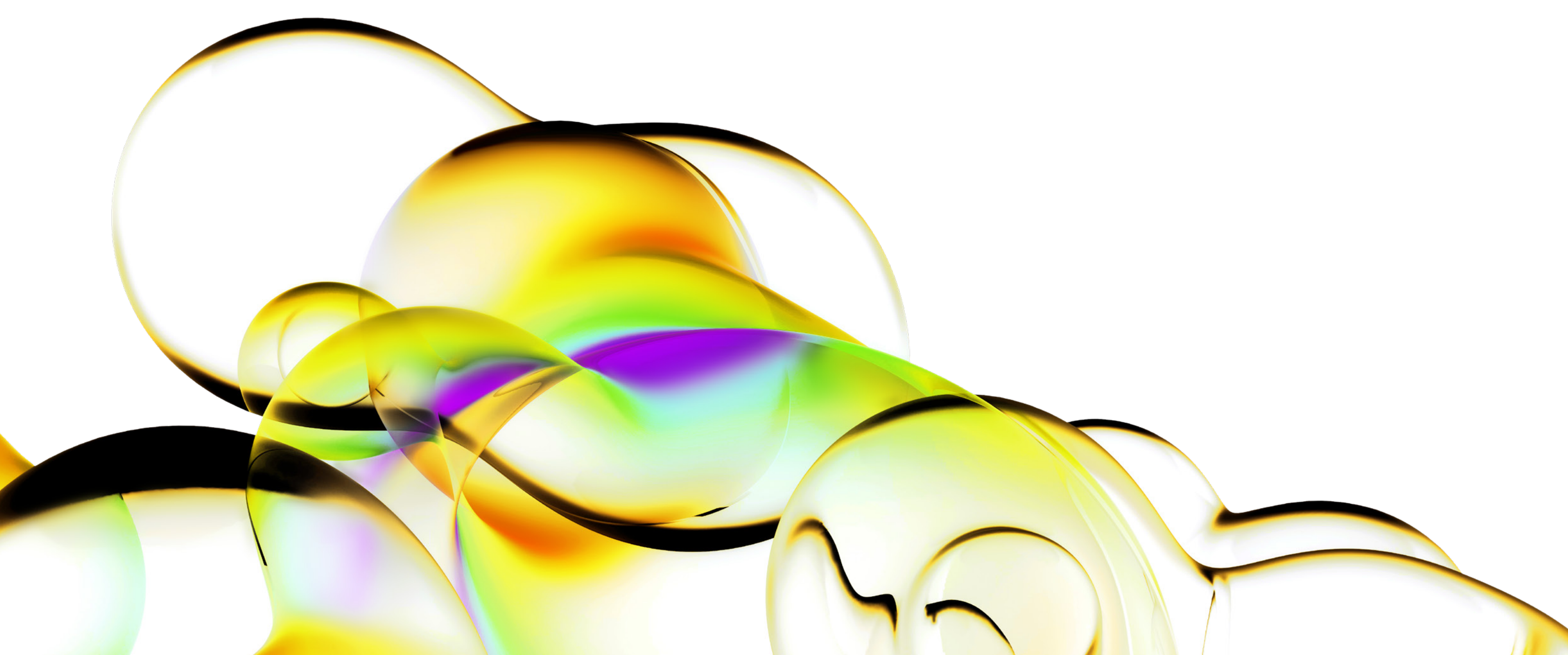
Dr. Ronald Edler
Revvity, Inc.

Introduction

The liquid scintillation measurement of biofuels and biomaterials in general has become routine in many laboratories in recent years and has also been carried out frequently in the Revvity application laboratory in Hamburg. This has so far resulted in the literature[1,2,3]. The measurement of biogenic materials is also described in detail in a recently published book on liquid scintillation technology.[4] Since the measurements of fuels involve natural radioactivity and only low counting rates are to be expected, the above-mentioned literature only described the use of very sensitive devices such as the Tri-Carb™ models 3170TR/SL and 3180TR/SL or the newer model of the Quantulus™ GCT 6220.

Especially with fuels, which in many cases have a carbon content of more than 80%, the count rates can be quite high if the amount of biogenic component is high or if, for example, the question is whether it is a pure biofuel or a mixture of bio- and fossil fuel. In the case of pure biofuel, the count rates are significantly higher than the background even in the very simple scintillation counters.

For this reason, the Tri-Carb 4910TR was used in normal count mode for such measurements. Comparative measurements were also carried out with the Quantulus GCT and will also be shown.



The measurement

Two different HVO (Hydrogenated Vegetable Oil) samples were used as fuel samples. The carbon content in these samples was determined to be 84% by means of elemental analysis. For the measurements, 11 ml of fuel were weighed with an analytical balance with an accuracy of 0.1 mg and dissolved in 10 ml of Ultima Gold F. A sample of 11 ml of fossil octane dissolved in 10 ml of Ultima Gold F was used as the background sample.

Table 1: Weight of sample

Sample	Mass	Mass carbon	tSIE
BKG	11 ml		619.66
JASMAR	8.0805 g	6.7876 g	641.26
EEMSTROOM	8.3594 g	7.0219 g	649.16

For some years now, the ^{14}C content of the atmosphere has again reached the levels of natural radioactivity in the pre-atomic age. This value was determined to be 13.56 DPM/g carbon +/- 0.7 DPM. The activities to be expected for 100% biogenic samples for the amounts of substance mentioned in Table 1 are listed in the table 2.

Table 2: Expected activity for 100% biogenic samples

Sample	Mass C	Activity
BKG	11 ml	0.00 DPM
JASMAR	6.7876 g	92.04 DPM
EEMSTROOM	7.0219 g	95.22 DPM

All samples were measured five times with a measurement time of 60 minutes each.

The external standard was measured with an error of 0.5% in the 2 σ confidence interval. All measurements in the Tri-Carb were carried out in the normal count mode. The evaluation was carried out in the open energy window of 0-156 KeV, in the optimized window of 8.5-92.5 KeV and with a PAC value of 200 in the optimized window of 7.0-93.0 KeV. For an explanation of the PAC value, see also the literature.[4, 5]

Table 3: Data measured with a Tri-Carb 4910 in NCM, PAC = Off, 0-156 KeV

Sample	CPMA	DPM1	Efficiency [%]	tSIE	FOM
BKG	18.27		95.21	627.42	
	17.95		95.16	618.79	
	17.47		95.15	617.35	
	17.93		95.16	618.03	
	19.15		95.15	616.72	
Average:	**18.15**	0.00	**95.17**	**619.66**	
JASMAR	109.00	95.34	95.29	641.26	
	108.17	94.46	95.30	643.29	
	107.95	94.24	95.29	641.51	
	108.88	95.21	95.29	641.83	
	105.27	91.44	95.28	641.02	
Average:	**107.85**	94.13	**95.29**	**641.78**	500.29
EEMSTROOM	107.13	93.34	95.33	649.48	
	109.48	95.81	95.32	648.25	
	106.72	92.92	95.32	647.76	
	109.45	95.77	95.33	648.80	
	109.03	95.32	95.34	651.51	
Average:	**108.36**	94.63	**95.33**	**649.16**	500.71

Table 3 is shown here for two main reasons. On the one hand, the good stability of the measuring instrument is to be shown here. This is not only important for the count rate, which of course must show the normal statistical deviation. A good stability of the quench parameter tSIE and thus a good stability of the counting efficiency obtained from the quench curve are particularly important.

The second reason is the fact that the first sample seems to have a slightly too high activity (+2.3%), while the second sample is very close to the expected value (–0.6%). Although all samples had been in the device for a few hours before the measurement started, the first sample still showed clear luminescence during the measurement. A problem that can occur with many fuel samples. Therefore, the sample conveyor should also remain closed during the measurements.

For this reason, but of course also to improve the sensitivity, the evaluation was carried out in an optimized window. This window was determined with the aid of the SpectraWorks software[8] and was between 8.5 and 92.5 KeV. The evaluation in this energy window is shown in Table 4.

As the new energy window only starts at 8.5 KeV, the luminescence in the sample is also eliminated. Luminescence is a very low-energy event and is observed in the energy distribution mainly in the range of 0-5 KeV. In addition, the significantly increased sensitivity can be recognized from the higher value for the figure of merit from Table 4.

The Sensitivity can be determined very precisely by calculating the decision threshold and the detection limit according to ISO 11929, a value that is easier to determine but still very helpful is the so-called figure of merit (FOM). The larger the value for the FOM, the more sensitive the measurement. The FOM will be determined from the counting efficiency squared divided by the background, FOM = E^2/B.

Table 4: Data measured with a Tri-Carb 4910 in NCM, PAC = Off, 8.5-92.5 KeV

Sample	CPMA	DPM1	Efficiency [%]	tSIE	FOM
BKG **Average:**	**8.60**	**0.00**	**80.39**	**619.66**	
JASMAR **Average:**	**83.32**	**92.38**	**80.88**	**641.78**	**760.7**
EEMSTROOM **Average:**	**86.24**	**95.80**	**81.04**	**649.16**	**763.7**

The first measurement now shows a significantly smaller deviation off +0.4%, the second measurement a deviation of +0.6%. Both results are excellent and better results are not to be expected because of the counting statistics which has an uncertainty of +/- 1.2% in the 2σ–confidence range even after 300 minutes of counting time. The reason for this improvement through the smaller measurement window is the elimination of luminescence. In addition, the value for the FOM has been significantly increased due to the smaller measurement window and thus the sensitivity has been improved. This is due to the significant reduction in the background, which more than compensates for the slight reduction in the counting efficiency.

In addition, measurements with the PAC value of 200 were also carried out in the Tri-Carb 4910TR, also in normal count mode. This value was not optimized but selected from experience. However, further optimization of this value is conceivable. For details on PAC values, see also the literature.[4, 5, 6]

The data obtained on the PAC value of 200 are shown in Table 5.

Table 5: Data measured with a Tri-Carb 4910 in NCM, PAC = 200, 7.0-93.0 KeV

Sample	CPMA	DPM1	Efficiency [%]	tSIE	FOM
BKG **Average:**	**6.08**	**0.00**	**80.39**	**616.78**	
JASMAR **Average:**	**80.56**	**92.42**	**80.59**	**642.97**	**1071.7**
EEMSTROOM **Average:**	**82.09**	**94.25**	**80.65**	**647.06**	**1073.0**

With the PAC value of 200, the background could be significantly reduced again, at the same time the counting efficiency was only slightly reduced, which significantly improved the FOM again.

Further measurements were carried out with identical samples on the Quantulus GCT 6220. The measurements with the Quantulus are shown in Table 6. Again, all samples were measured with a measuring time of 60 minutes and 5 repetitions.

Table 6: Data measured with a Quantulus GCT 6220, NCM, GCT = Off, 0-156 KeV

Sample	CPMA	DPM1	Efficiency [%]	tSIE	FOM
BKG	4.57	0.00		626.00	
JASMAR	92.73	93.55	94.23	628.88	1943.0
EEMSTROOM	94.45	95.35	94.26	634.27	1944.2

The measurements on the Quantulus also show the expected activities with only minor deviations that are within the statistical deviations. The sensitivity of the Quantulus is, however, significantly better even in normal count mode in the open window, as the background is considerably lower due to the guard detector in the device. The evaluation in the optimized window of 18.5-84.5 is shown in Table 7 with GCT = Low.

Table 7: Data measured with a Quantulus GCT 6220, NCM, GCT = Low, 18.5-84.5 KeV

Sample	CPMA	DPM1	Efficiency [%]	tSIE	FOM
BKG	0.51	0.00		626.00	
JASMAR	88.72	93.63	94.21	628.88	> 2000
EEMSTROOM	90.44	95.43	94.24	634.27	> 2000

The optimization of the energy window on the Quantulus in combination with GCT leads to a further significant increase in sensitivity. When using the GCT technology[4] for background correction, the simple formula for the FOM cannot be used, as it is no longer a normal distribution. However, due to the strong correlation of the data, a factor of 0.4 to 0.5 can be calculated from which a FOM of well over 2000 is obtained.

The results show the significantly better sensitivity of the Quantulus GCT 6220, but it also becomes clear that samples with high proportions of biogenic materials can also be measured very well with a simple Tri-Carb.

Especially samples with biogenic proportions of 50-100% can be measured very well with a Tri-Carb in normal count mode. Samples with contents of 20-50 percent can also be measured in a Tri-Carb but better with High Sensitivity or Low Level Mode. A Tri-Carb with Low Level Count Mode or a Quantulus GCT 6220 is recommended for samples below 20% biogenic content. With the same biogenic content, the latter can achieve the same detection limit in a shorter measuring time than a Tri-Carb with low level count mode. These %-values are only recommendations and of course strongly depend on the sample. In particular, samples with severe colour quenching, such as some biodiesel samples, may require the use of diluted samples and/or more sensitive measuring devices.

If, on the other hand, colored samples are decolorized and enriched using the benzene synthesis[4], an ideal sample is available, which in many cases can then be analyzed with a Tri-Carb.

Measurement of fuels with 10% biogenic content

Since the measurement of purely biogenic fuels with the Tri-Carb has worked very well, samples with a lower content should also be measured. For this purpose, 3 samples from a Hamburg company were measured, which should contain a sample with 100% and two samples with 10% biogenic content each. The weighed amounts of these samples are shown in Table 8.

Again, all samples were measured five times with a measurement time of 60 minutes each. A sample with 11 ml octane in 10 ml Ultima Gold F was again used as the background sample, but it was quenched with nitromethane until the tSIE was of the same order of magnitude. Only a few microliters were required for this. As with the samples above, all samples were made in 2020. For this reason, purely biogenic samples should again contain an activity of 13.56 DPM/g carbon.

Table 8: Sample weight and expected activity of the sample

Sample	Mass [g]	Carbon content [%]	Mass C [g]	Biogenic content [%]	Expected activity [DPM]	tSIE
BKG	11 ml	-	-	0	0.00	583.14
40039459	7.6422 g	83.99	6.4187	100	87.04	554.75
40039460	7.6007 g	84.11	6.3930	10	8.67	545.58
40039461	7.6871 g	85.99	6.6101	10	8.96	571.93

Table 9: Determined activity and biogenic content, 7,5-77,0 KeV, PAC=Off

Sample	CPM	Net CPM	Counting efficiency [%]	DPM	Measured biogenic content [%]
BKG	8.17	0.00	-		
40039459	78.11	69.94	79.92	87.51	100.5
40039460	15.32	7.15	79.90	8.95	10.3
40039461	15.76	7.59	79.95	9.49	10.6

The counting efficiencies in Tables 8 and 9 were again determined using a quench curve with the tSIE as the quench parameter. The deviations from the expected activities are between 0.3 and 0.6% and thus in the uncertainty of the measurement to be expected from the counting statistics in 300 minutes of measurement time. This measurement also shows that a Tri-Carb can also determine biogenic contents of approx. 10% very well in normal count mode. It should be mentioned here, however, that all biogenic samples that were measured for this application note were almost colorless or only caused a very weak yellow color. Such samples are ideal samples because they allow low quenching and thus high-count rates and good counting statistics. The measuring time in the Tri-Carb could be reduced with the same quality of the results if the scintillation counter is equipped with the High Sensitivity Count Mode.

Literature

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