METHYL SALICYLATE AS A MEDIUM FOR RADIOASSAY OF ^{36}CHLORINE USING A LIQUID SCINTILLATION SPECTROMETER

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Abstract

Methyl salicylate (MS), a high refractive index liquid with wave-shifting properties, has been used as a Cerenkov radiation generating medium for the radioassay of ^{36}Cl by liquid scintillation (LS) spectrometer. Comparative experiments, using both a standard toluene-based LS fluor and toluene alone, for the measurement of ^{36}Cl were undertaken. The methyl salicylate medium was found to perform at an intermediate counting efficiency, near that for the LS fluor. In the presence of moderate amounts of nitromethane, the MS was less susceptible to chemical quenching effects than either the fluor or toluene.

Counting efficiencies for ^{36}Cl in MS, toluene and toluene fluor respectively were 82.4, 28.4 and 100.3 percent with a Picker Liquimat 220 LS spectrometer, and 91.6, 54.9 and 100.0 percent with a Searle Mark III LS spectrometer. The addition of nitromethane (11.3 percent of final volume) reduced these efficiencies to 50.5, 10.0 and 15.4 percent, and to 58.8, 12.4 and 19.0 percent, respectively.

The data are discussed in relation to observed changes in the pulse height spectra. Chemical quench correction by ESCR and by SCR methods is reported.

Introduction

The use of liquid scintillation (LS) counters for the measurement of Cerenkov radiation emitted upon the deceleration of highly energetic β particles in liquid media has become increasingly popular over the past several years.[1] The technique has found particular acceptance as an alternate to LS counting of samples which contain appreciable quantities of substances which chemically quench the LS process. Many liquids have been used as Cerenkov generating media, particularly water, and organic solvents with refractive indices considerably greater than the refractive index of water. In addition, Cerenkov generating systems containing wave-shifting chemicals have been developed. These systems, although no longer purely Cerenkov generators, have provided improved counting efficiencies.[1,2]

This paper describes the performance characteristics of methyl salicylate (MS-C) as a Cerenkov generator for the radioassay of ^{36}Chlorine. This high refractive index liquid posesses wave-shifting properties, absorbing the ultraviolet emissions of the Cerenkov spectrum, and re-emitting photons in that visible portion of the electromagnetic spectrum to which the photomultiplier tubes are more sensitive. Comparisons are drawn to the characteristics of Cerenkov counting of ^{36}Cl in toluene (T-C), and to LS counting of ^{36}Cl in toluene containing PPO and POPOP.

Experimental

Methyl salicylate (laboratory grade, Fisher Scientific Co., Edmonton) was distilled before use. Scintillation grade toluene, PPO and POPOP (Fisher Scientific Co., Edmonton) were used as supplied. The LS fluor was prepared to contain PPO (4 g l^{-1}) and POPOP (50 mg l^{-1}) in toluene.

Commercial LS glass vials (Kimble, Toledo, Ohio) were used for all procedures. Ten ml of the appropriate counting medium was pipetted into each vial; these vials were then scintillation counted to assure absence of contamination and photo or chemiluminescence effects. Standard (±3%) ^{36}Cl-Chlorobenzene (50 µl; 4.17 x 10^5 dpm ml^{-1}; New England Nuclear, Boston) was added to each vial by microsyringe, after which the individual vials were scintillation counted again to determine the absolute counting efficiency. The LS counting of each vial was repeated after each subsequent addition of small volumes of nitromethane (Reagent grade, Fisher Scientific Co., Edmonton).

Vials were scintillation counted in a Liquimat 220 LS spectrometer (Picker Nuclear, New York) and in a Mark III LS spectrometer (Searle Instrumentation, Chicago). Pulse height spectra obtained from the Liquimat 220 LS spectrometer were stored in either a Nuclear Chicago Model 25601 multichannel analyzer (MCA) or in a Northern Scientific NS 636 MCA.

Results

Methyl salicylate was found to give high counting efficiency for ^{36}Chlorine in the absence of chemical quenching agents using both the 'new generation' Mark III LS counter, and the older Liquimat 220 instrument. The superiority (E^2/B) of MS over the standard LS fluor, although apparent in the absence of nitromethane quench, became increasingly evident as the concentration of nitromethane exceeded 1 percent. At maximum quench, MS-C counting was three times as efficient as LS counting. The T-C counting was much less efficient than either the LS or MS-C process, with or without chemical quench. Of particular interest was the large decrease in counting efficiency upon addition of small amounts (10 μl; 0.1%) of nitromethane. Counting efficiencies, background count rates, and E^2/B values, are shown for the LS, MS-C and T-C systems using both liquid scintillation counters, in Table 1.

Quench correction by 'external standard pulse' (ESP) and sample channels ratio (SCR) was investigated using the programmed 'windows' of the Mark III spectrometer. The ESP method was found to perform well in moderately quenched LS samples, but to be unsatisfactory for MS-C and T-C samples. The dynamic range of SCR provided by programmed windows was found to be adequate for the entire range of quench in MS-C and T-C samples, but was very limited for LS samples in both programs 2 (^{14}C) and 10 (^{36}Cl). In addition, the use of program 10 led to the exclusion of large numbers of pulses, resulting in unnecessarily low counting efficiencies at severe quench levels. Quench correction data are given in Figures 1 and 2.

The pulse height spectra (PHS) depicted in Figure 3 show major differences from each other. The comparatively broad PHS of the MS-C system is noteworthy. The ^{137}Cs compton electron induced Cerenkov spectrum in MS (Figure 4) is seen to match closely the unquenched MS-C ^{36}Cl PHS. The external standard count rate (∿ 120,000 cpm) observed with the unquenched MS-C generator was adequate to provide acceptable statistical precision. Even with the significant loss of counts with severe quenching the method would be useful. External standard channel ratios obtained are listed in Table 2.

Discussion and Conclusions

The efficacy of methyl salicylate as a liquid Cerenkov radiation generating medium for ^{36}Cl has been shown to approach that of a typical LS system in terms of unquenched sample counting efficiency, and to surpass the LS system

Table 1. Observed counting efficiencies for ^{36}Cl in LS fluor (PPO/POPOP/toluene), methyl salicylate (MS-C) and toluene (T-C) with increasing quantities of nitromethane. Measurements were made with the Picker Liquimat 220 and the Searle Mark III LS spectrometer.

Volume CH_3NO_2 (μl)	LS 220[1]	LS Mk III[a]	MS-C 220[2]	MS-C Mk III[b]	TC 220[3]	TC Mk III[c]
0	100.3	100.0	82.4	91.6	28.4	54.9
10	100.0	99.6	81.6	90.5	19.4	30.7
20	100.0	99.4	80.9	89.7	17.3	25.3
40	98.4	98.9	79.4	88.3	16.0	21.6
80	94.5	96.4	77.2	86.3	14.3	19.0
160	85.4	86.8	74.3	83.0	13.4	17.1
320	54.5	61.4	69.5	79.6	12.7	15.6
640	27.2	32.0	61.6	70.0	11.6	14.2
1280	15.4	19.0	50.5	58.8	10.0	12.4
B	141.0	48.8	88.7	25.0	46.0	24.4
E^2/B	71.3	204.9 572.6[d]	76.5	335.6	17.5	123.5

1. window 10-1000
2. window 10-650
3. window 10-450

a. P-32 window, Program 4
b. C-14 window, Program 2
c. H-3 window, Program 1
d. Cl-36 window, Program 10

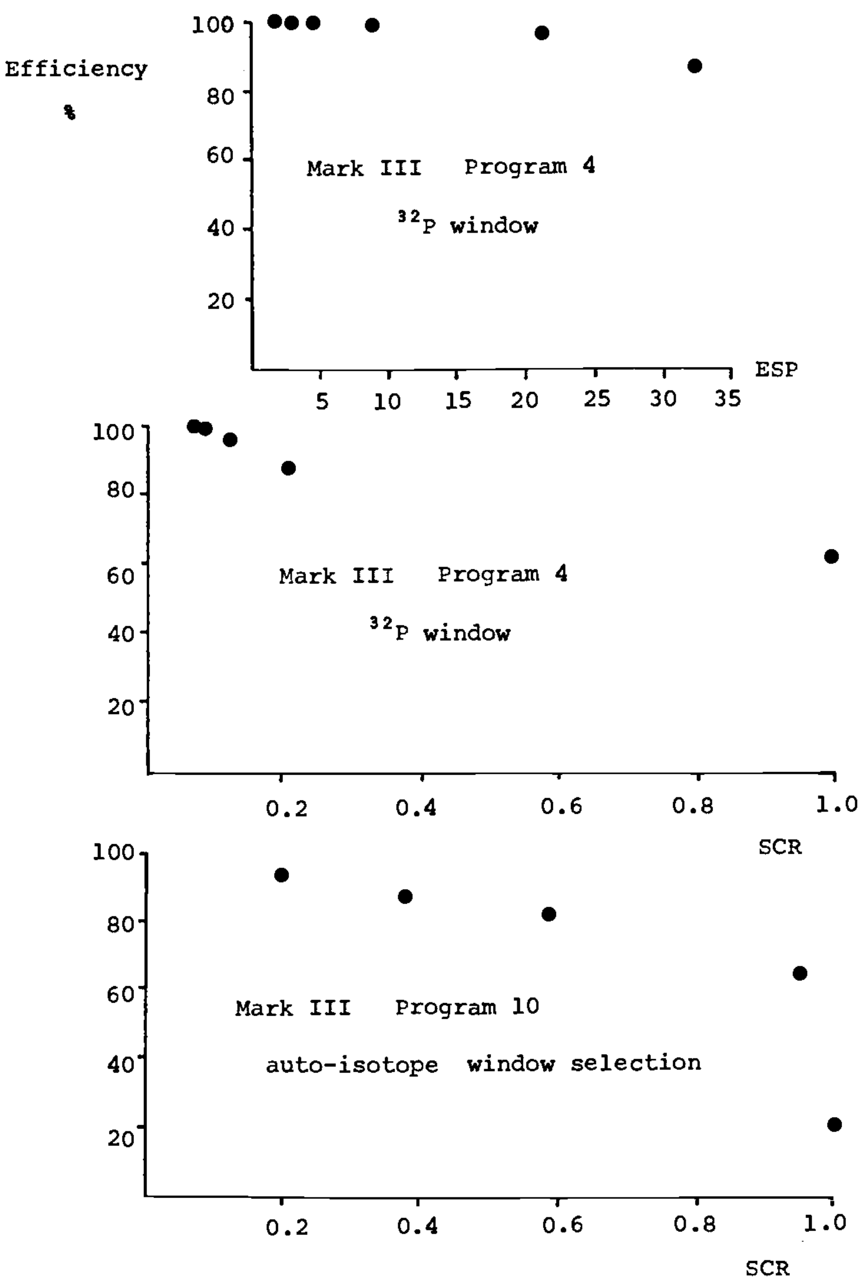

Figure 1. Quench correction for ^{36}Cl in Toluene/PPO/POPOP using the ESP and SCR methods.

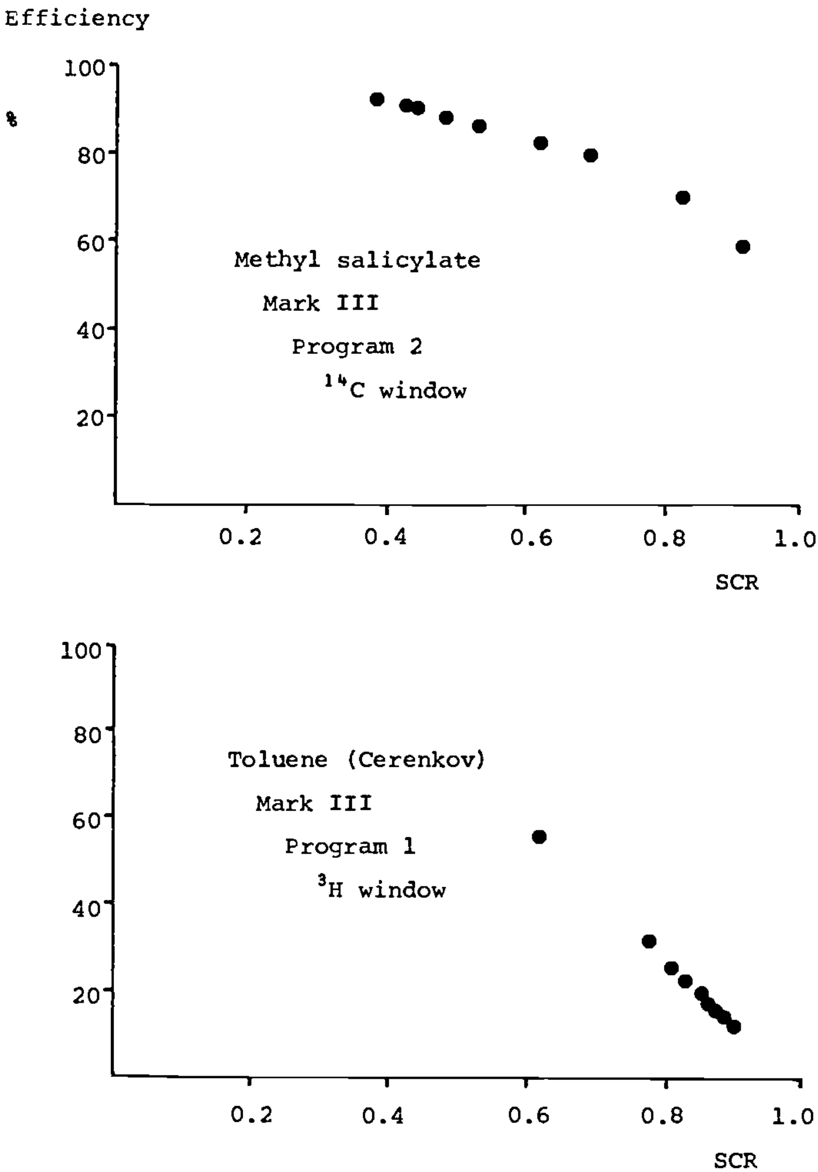

Figure 2. Quench correction for ^{36}Cl in methyl salicylate (MS) and toluene (T) using the SCR method.

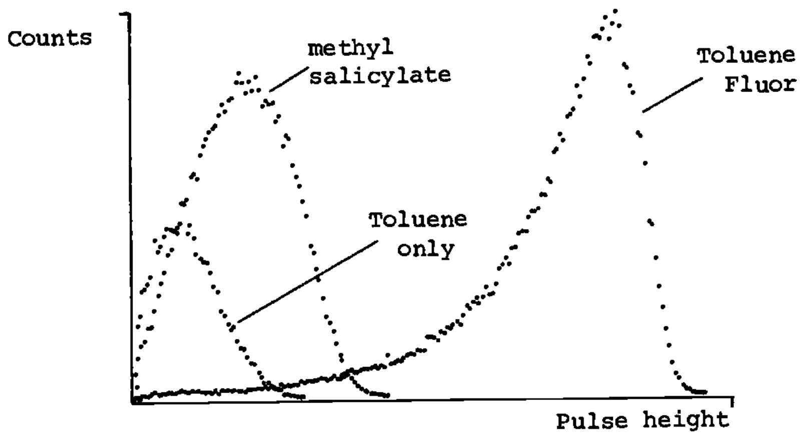

Figure 3. Pulse height spectrum of ^{36}Cl in various media.

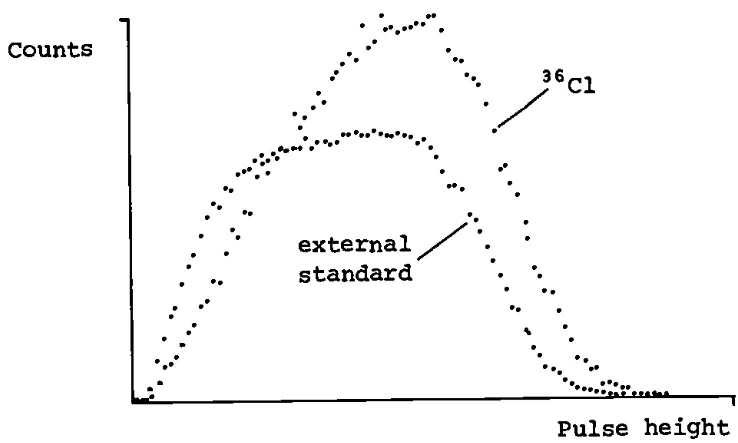

Figure 4. Pulse height spectrum in methyl salicylate of ^{36}Cl and the Liquimat 220 ^{137}Cs external standard.

Table 2. External standard channels ratio (ESCR), external standard counts, and percent efficiency for ^{36}Cl in methyl salicylate, using the Picker Liquimat 220 LS spectrometer.

Volume of CH_3NO_2	Relative % efficiency	Counts in D	Counts in C	ESCR D/C
0	100.	31558	25772	1.241
10	97.4	29234	26417	1.105
20	96.1	29228	28086	1.058
40	94.3	26546	28320	0.937
80	90.8	24564	29152	0.842
160	85.3	20526	29303	0.742
320	78.1	16802	29259	0.607
640	68.3	11439	27065	0.431
1280	53.1	6648	23386	0.287

D = 125-420

C = 10-180

with respect to resistance to severe chemical quench. Examination of the PHS for ^{36}Cl in MS and toluene suggests that the high counting efficiencies observed in MS are attributable to the wave-shifting characteristics of that liquid. The photon wave-lengths are shifted from the ultraviolet region to the visible region, thereby decreasing absorption of photons by the solvent and by the glass of vials and photomultiplier tube (PMT) faces. Furthermore, wave-shifted photons have isotropic spacial distribution, thereby increasing the detection efficiency in typical LS spectrometers in which the PMTs are at an angle of 180° to each other and are operated in coincidence.[3] The higher refractive index of MS (1.522 vs 1.494 for toluene)[4] should also increase the photon yield[5] by decreasing the Cerenkov threshold level. Inspection of the ^{36}Cl beta energy spectrum reveals that approximately 65% of the β^- particles have energies above the calculated Cerenkov threshold for β particles in MS. In view of the very high counting efficiency that has been observed (91.6%) it would appear that the refractive index of MS at the Cerenkov wavelengths is indeed greater than 1.522 (R.I. Na_D^{20}).

Quench correction by SCR has been found to be satisfactory in the MS-C and the T-C systems using the programmed windows (2-^{14}C; 1-^{3}H, respectively) of the Searle Mark III LS spectrometer. The small dynamic range observed for both ESCR and SCR methods in the LS analysis could undoubtedly be remedied by more appropriate window selection than that presented. The loss of counts experienced when using a ^{36}Cl LS standard to set Program 10 windows of that spectrometer could similarly be reduced. The use of the SCR method with the Liquimat 220, although not investigated, would in all likelihood be useful for quench correction through appropriate channel selection. Quench correction by ESCR using ^{137}Cs external standard should be ideal because of similarities in the PHS for ^{137}Cs compton electrons and ^{36}Cl β particles in MS.

As pointed out previously[1], the inclusion of wave-shifting compounds in Cerenkov generating media produces a system which is no longer purely Cerenkov in nature. In MS-C counting, however, it is not apparent that significant chemical quenching does occur, as the rate of decline of counting efficiency remains at 1% or less per 10 μl of nitromethane added, up to the maximum added (1280 μl per 10 ml MS). This small rate of decline may in fact be primarily due to a decrease in the refractive index of MS (RI = 1.522) by addition of nitromethane (RI = 1.380[4]), and the absorption of photons by nitromethane.

The T-C data show a similar slow decline in counting efficiency, but only after addition of 10-20 µl of nitromethane. In this case, it would appear that the initial large decreases in counting efficiency are due to chemical quenching of the scintillation process in toluene, a solvent which has an appreciable photon yield itself.[6] Subsequent decreases (after 20 µl of nitromethane) are in the order of 1% or less, similar to those observed in MS.

References

1. H.H. Ross and G.T. Rasmussen, in Liquid Scintillation Counting: Recent Developments, P.E. Stanley and B.A. Scoggins (Eds.), Academic Press, N.Y. (1974) p. 363.
2. R.P. Parker and R.H. Elrick, in The Current Status of Liquid Scintillation Counting, E. Bransome (Ed.), Grune and Stratton, N.Y. (1970) p. 110.
3. H.H. Ross, in Organic Scintillators and Liquid Scintillation Counting, D.L. Horrocks and C.T. Peng (Eds.), Academic Press, N.Y. (1971) p. 757.
4. Handbook of Chemistry and Physics, R.C. Weast and S.M. Selby (Eds.), The Chemical Rubber Co., Cleveland, Ohio, 47th Edition (1966/67) p. E151.
5. I.M. Frank and I.G. Tamm, Dokl. Akad. Nauk. SSSR 14, 109 (1937).
6. D.L. Horrocks, Applications of Liquid Scintillation Counting, Academic Press, N.Y. (1974) p. 19.