

Chapter 11

The Use of Heavy Metal Loaded Scintillators for Counting Electron Capture Radionuclides in the Presence of Tritium

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INTRODUCTION

The assay of doubly labelled samples containing tritium and iodine-125 was discussed at the last symposium in 1975¹. Attention was drawn to the fact that use of a double instrument method (γ -counter + liquid scintillation counter) could result in erroneous data. Use of a conventional sodium iodide crystal γ -counter to measure the very weak emissions from electron capture nuclides such as iodine-125 can be subject to errors arising from variable sample self-absorption. For example, addition of 0.5% sodium iodide carrier to an ¹²⁵I sample caused a reduction in count-rate of around 5%. Unlike the liquid scintillation counter, there is no simple way to monitor the counting efficiency of samples in a γ -counter.

In liquid scintillation counting the problems arising from spectral overlap are well known and are particularly troublesome with tritium and iodine-125. However, these difficulties were alleviated by a new technique involving the use of an organotin additive. The additive had a twofold effect: firstly, it caused normal impurity quenching of the tritium count-rate but secondly, it caused a considerable enhancement of the iodine-125 count-rate. Thus, by counting doubly labelled samples in the absence and then again in the presence of organotin compound it was possible to set up a pair of simultaneous equations which could be solved for the separate activities of the two isotopes.

For the initial experiments samples were counted in homogeneous solution in a toluene-based scintillant. Shortly afterwards, however, results were published³ which showed that a similar enhancement of iodine count-rate could be obtained with inorganic lead or thallium salts in aqueous systems using micellar scintillants containing Triton X100 or Instagel.

The work reported in this paper described further investigation of suitable additives and the possibilities for extending the method to systems involving other electron capture nuclides.

EXPERIMENTAL

Sodium¹²⁵I iodide, sodium⁷⁵Se selenite, [⁵⁷Co]cobaltous chloride, [⁵¹Cr] chromic chloride, [³H]water and [³H]n-hexadecane were obtained from the Radiochemical Centre, Amersham, England. [¹²⁵I]iodobenzene was prepared as described previously. Homogeneous samples were counted in toluene solution containing butyl-PBD (0.8%). Aqueous samples were counted in a micellar scintillator NE260 (Nuclear Enterprises Ltd., Edinburgh, Scotland) containing a constant amount (10%) of aqueous solution. The additives were commercial samples used without further purification. The counting equipment was supplied by Nuclear Enterprises Ltd. and consisted of a liquid scintillation sample changer (NE 8316) interfaced with a multichannel analyser

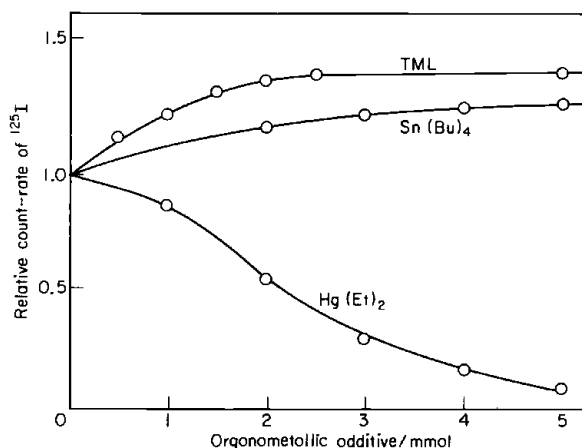


Fig. 1. The effects of adding organometallic compounds to homogeneous counting samples containing ^{125}I iodobenzene.

(Tektronix 603) and a small computer (Digital Equipment PDP 11/05). Pulse height spectra were recorded directly from the screen of the multichannel analyser using a Polaroid camera. The system was installed in a temperature controlled room at 20°C .

RESULTS AND DISCUSSION

1. Iodine-125

The choice of organometallic additives was decided largely by solubility or availability. The phenyl derivatives of tin, mercury and lead were all relatively insoluble in toluene and therefore could not be examined. Figure 1 shows the results of adding successive quantities of tetramethyl lead (TML), tetrabutyl tin or diethyl mercury to homogeneous counting samples of ^{125}I . A 35% increase in count rate was obtained using TML at much lower concentrations than the tin compound. The results for diethyl mercury indicate that the effect is not obtained simply by loading the scintillator with heavy metal otherwise there would have been little difference between the lead ($Z = 82$) and mercury ($Z = 80$) compounds. For the micellar ^{125}I scintillator the effects of various additives on the count-rate of sodium ^{125}I iodide are shown in Fig. 2. Here again TML resulted in a considerable enhancement of

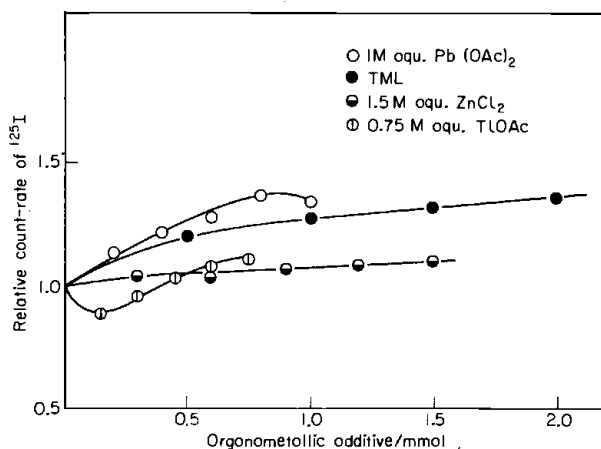


Fig. 2. The effects of various additives on the count-rate of sodium ^{125}I iodide solutions in micellar scintillator.

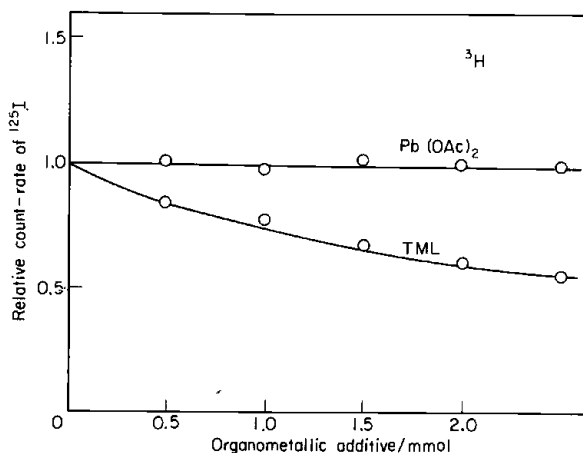


Fig. 3. The effects of additives on the count-rate of tritium samples in micellar scintillator.

counting rate as did lead acetate solution up to the point where precipitation commenced at around 10% of 1M solution. The results with thallium acetate were disappointing but not very surprising as a slight yellow precipitate was observed. Zinc chloride solution was examined as it had previously been said to enhance count rates for ^{125}I (see discussion, Ref. 1). In the present system it had little effect.

From this rather limited survey it was concluded that the two most promising additives were TML and aqueous lead acetate solution. The overall enhancement of ^{125}I count-rate was much the same for the two additives despite the fact that they were present in different phases in the micellar scintillator. However, when their effect on the count-rate of tritium samples was examined the importance of the phase was immediately apparent. Figure 3 shows the results obtained when counting tritium in the micellar scintillator. Lead acetate had no quenching effect at all whereas the TML which was dissolved in the organic (scintillator) phase was a strong quenching agent. These results were obtained for both tritiated water and tritiated *n*-hexadecane i.e. they did not depend upon which phase the tritium was dissolved in. The differences between the two phases are further illustrated by reference to photographs of the pulse height spectra. Figure 4 is the pulse height spectrum for an unquenched tritium sample. The marker has been placed at channel number 65 which is well above the cut-off point for the tritium spectrum. This marker is retained in the

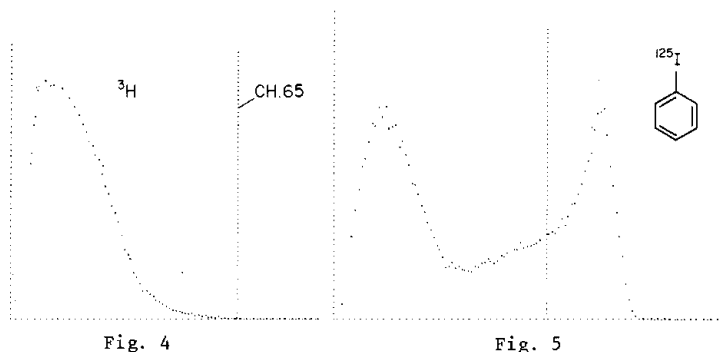


Fig. 4. The pulse height spectrum of an unquenched tritium sample.

Fig. 5. The pulse height spectrum of ^{125}I as iodobenzene in homogeneous toluene-butyl PBD scintillator.

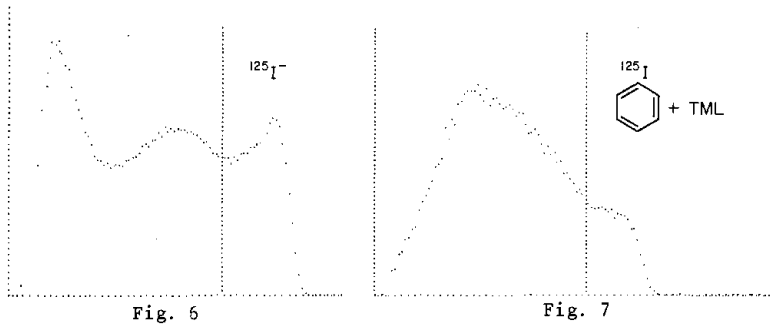


Fig. 6. The pulse height spectrum of ^{125}I as sodium iodide in micellar scintillator.

Fig. 7. The pulse height spectrum of ^{125}I in homogeneous toluene-butyl PBD scintillator plus 2 mmol TML additive.

same position on all subsequent figures. Figures 5 and 6 show the spectrum of ^{125}I in homogeneous toluene solution and in micellar scintillator respectively. Both show a substantial peak in the tritium region due to the 3-4 keV Auger and internal conversion electrons and a second peak due to the higher-energy internal conversion electrons and a small number of photo and Compton scattered electrons from interactions of the 27-35 keV X-rays and γ -rays with the scintillator. The slight quenching effect of the surfactant and water in the micellar scintillator is illustrated by the shift to lower energies shown in Fig. 6. Figure 7 shows the effect of adding TML to a homogeneous counting sample. Quenching of the lower energy pulses is apparent but this is obviously more than offset by an increase in pulses in the middle energy range which are due to interactions of the X-rays and γ -rays with the electron dense lead atoms. The spectrum for the micellar scintillator containing TML was very similar to Fig. 7. However, addition of lead acetate gave a rather different picture as shown in Fig. 8. Here the absorbing material was in the aqueous phase and resulted in enhancement of the higher energy peak from scattered electrons without quenching of the lower energy pulses.

If ^{125}I is to be counted alone then there are obvious advantages in the use of aqueous lead salts to enhance the counting rate and no doubt systems could be devised which would tolerate higher concentrations than were possible in the present work. If, however, doubly labelled samples are to be assayed then TML must be the preferred additive since it gave a much greater relative change in the counting efficiencies of the two isotopes. Tetramethyl lead is preferred over the organotin compounds since it is required in lower concentrations, it is much cheaper to buy and is sold as a ready prepared solution in toluene.

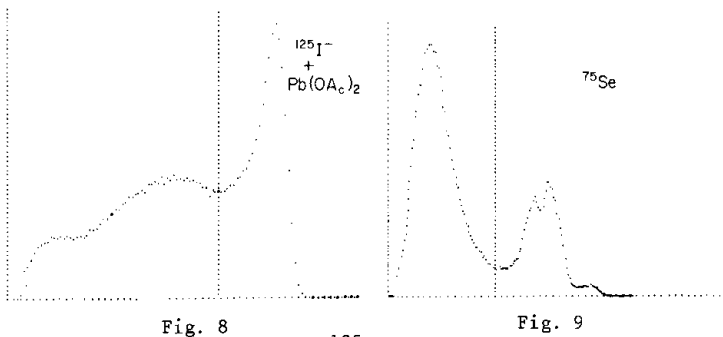


Fig. 8. The pulse height spectrum of ^{125}I in micellar scintillant plus 0.8 mmol $\text{Pb}(\text{OAc})_2$.

Fig. 9. The pulse height spectrum of ^{75}Se in micellar scintillator.

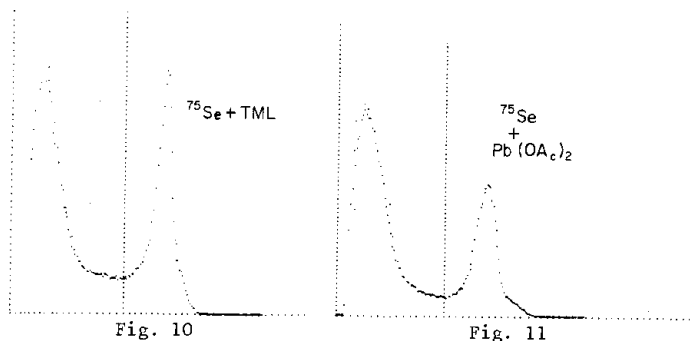


Fig. 10. The pulse height spectrum of ^{75}Se in micellar scintillator plus 2 mmol TML.

Fig. 11. The pulse height spectrum of ^{75}Se in micellar scintillator plus 0.8 mmol $\text{Pb}(\text{OAc})_2$.

2. Other electron capture radionuclides

The main feature associated with the decay of electron capture nuclides is that, as a result of the capture process, a vacancy occurs in the K or possibly the L electron shell of the new atom. When this vacancy is filled by an electron from another shell there is an energy emission equivalent to the binding energy of the captured electron. This energy takes the form of very weak (3-10 keV) X-rays or resultant Auger electrons and these radiations give rise to a substantial peak in the liquid scintillation spectrum in the same region as tritium. Selenium-75, cobalt-57 and chromium-51 all have additional higher energy γ -radiations associated with their decay processes and it was thought that electron dense additives might enhance count rates due to these nuclides.

Figure 9 illustrates a typical pulse height spectrum for ^{75}Se in micellar scintillator. The large peak in the tritium region is obvious but there were other peaks due to the various γ -rays which occurred outside this region. Figures 10 and 11 show the effects of added TML and lead acetate respectively. There was an apparent enhancement of the higher energy peaks. Unfortunately the spectra are deceptive since, as shown in Fig. 12, neither the total count rate nor the higher energy count-rate (above the tritium cut-off) was significantly enhanced by either additive.

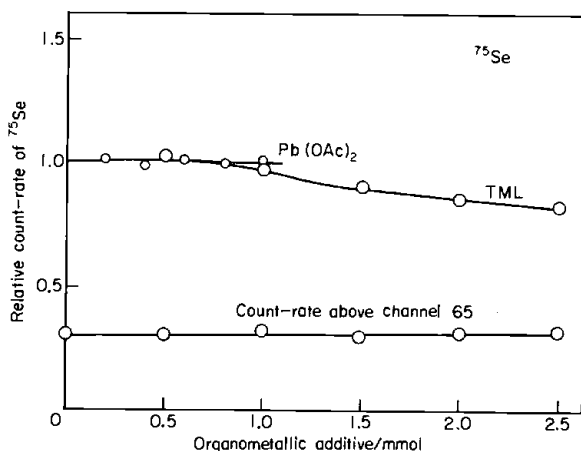


Fig. 12. The effects of additives on the count-rates of ^{75}Se samples in micellar scintillator.

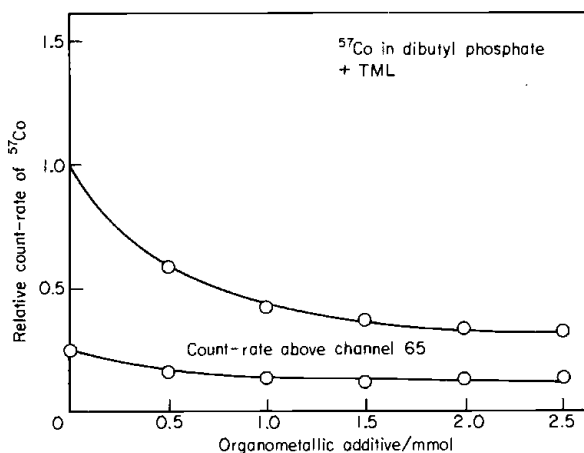


Fig. 13. The effects of adding TML to homogeneous counting solutions of ⁵⁷Co in dibutyl phosphate-toluene-butyl PBD scintillator.

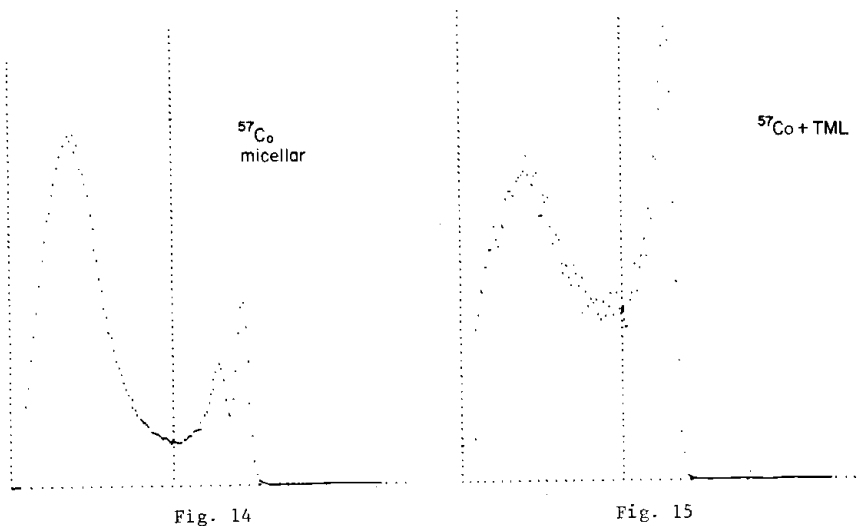


Fig. 14. The pulse height spectrum of ⁵⁷Co in micellar scintillator.

Fig. 15. The pulse height spectrum of ⁵⁷Co in micellar scintillator plus 2 mmol TML.

In the case of cobalt-57, homogeneous counting was attempted by extracting the isotope into dibutyl phosphate which was then included as a 5% solution in the toluene-butyl PBD scintillator. Unfortunately, as Fig. 13 shows, addition of TML had only adverse effects on the count-rate. In the micellar scintillator the effect was rather better. Figure 14 shows the pulse height spectrum and Figs 15 and 16 show the effects of adding TML and lead acetate respectively. In each case there was an apparent enhancement of the higher energy peaks but again, as Fig. 17 shows, the effects were very minor.

Finally, Fig. 18 shows a typical spectrum for chromium-51 with its very low energy peak due to the 5 keV vanadium X-rays and a small higher energy peak due to a γ -ray which has an abundance of only 9%. Figure 19 shows that this nuclide behaves very much like tritium and is quite heavily quenched by TML.

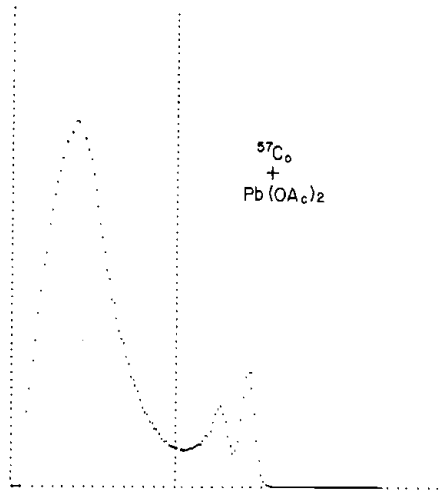


Fig. 16. The pulse height spectrum of ^{57}Co in micellar scintillator plus 0.8 mmol $\text{Pb}(\text{OAc})_2$.

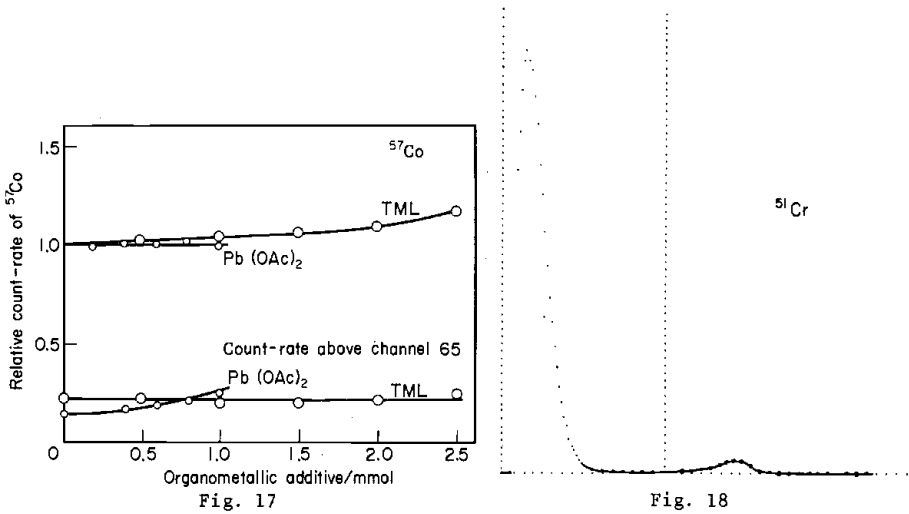


Fig. 17. The effects of additives on the count-rates of ^{57}Co samples in micellar scintillator.

Fig. 18. The pulse height spectrum of ^{51}Cr in micellar scintillator.

CONCLUSIONS

The use of lead-loaded liquid scintillators for either homogeneous or micellar counting of iodine-125 has been shown to result in substantial improvement of counting efficiency. For the assay of samples doubly labelled with tritium and iodine-125 tetramethyl lead was shown to be the most suitable additive since it caused the greatest relative change in the counting efficiencies for the two isotopes.

In the case of selenium-75 and cobalt-57 the additives had little effect on count rates. However, use of tetramethyl lead for the assay of doubly labelled samples of either

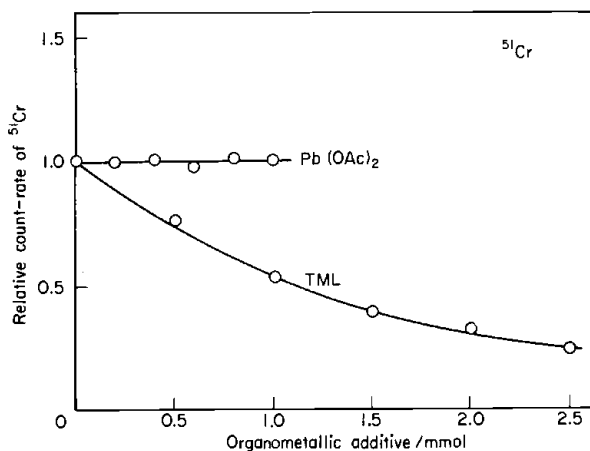


Fig. 19. The effects of additives on the count-rates of ^{51}Cr samples in micellar scintillator.

of these isotopes with tritium might be feasible since a substantial change in tritium counting efficiency resulted at concentrations where the electron capture nuclide efficiencies remained constant.

For chromium-51 the use of additives caused severe quenching and this nuclide behaved in a similar fashion to tritium. Assay of doubly labelled samples would thus require chemical separation of the two isotopes.

ACKNOWLEDGEMENT

I am grateful to Dr J. Chapman for helpful suggestions during the course of this work.

REFERENCES

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DISCUSSION

B.E. GORDON: In what form was the tritium when studying the effect of TML and Pb(OAc) $_2$? In both the aqueous and the oil soluble forms, was there any difference between the effect of TML? I suspect that TML is simply a quencher of the energy transfer process from solvent to solute and so would have the same effect whether in colloid or homogeneous systems.

The effect of TML on ^{125}I is a combination of quenching and increased γ -ray absorption with the former predominating. If this is correct, Pb(OAc) $_2$ would be a greater enhancer since it is not a quencher. However, if the γ -ray is totally absorbed in the aqueous phase, no count will result unless the electron (photoelectron) can reach the oil phase.

G. AYREY: Tritium was in the form of tritiated water or tritiated *n*-hexadecane. The effects were identical in each case. In general we agree with your explanations of the observed phenomena.