

Development of a Reference Liquid Scintillation Cocktail

WM VAN WYNGAARDT 1 AND P CASSETTE 2

¹Radioactivity Standards Laboratory, CSIR National Metrology Laboratory, 15 Lower Hope Road, Rosebank, Cape Town 7700, South Africa ²LNE-Laboratoire National Henri Becquerel, 91191 Gif-sur-Yvette cedex, France Email: fvwyngaardt@csir.co.za

ABSTRACT

Accurate and internationally recognised radionuclide standards are important for the nuclear industry. It is thus necessary for national laboratories preparing such radioactivity measurement standards to demonstrate equivalence to other national laboratories. A reference system which would allow laboratories to compare their activity measurements of non-gamma-emitting radionuclides at any time is currently being developed by the ESIR (Extended International Reference System) working group of the Consultative Committee for Ionizing Radiation CCRI(II). The system will be maintained at the International Bureau of Weights and Measures (BIPM), France. The system requires a non-commercial reference liquid scintillation cocktail, the development of which is described here. A number of cocktails were tested for their ability to mix with 1 % aqueous solution and for 3H counting efficiency. Three of the most promising cocktails were further tested with seven different radionuclides. The best results were obtained with a cocktail consisting of p-xylene, 2-phenoxyethanol, PPO and bis-MSB. This cocktail gave reasonable counting efficiencies and stable sources for all radionuclides tested (3H, 63Ni, 14C, 55Fe and 36Cl) except for the strontium-based ones (89Sr, 90Sr/90Y). Although the cocktail gave acceptable results, further development will be undertaken to also provide stable strontium counting sources. In addition, the aim is to optimise the pxylene/2-phenoxyethanol ratio in terms of detection efficiency and source stability.

INTRODUCTION

in soluble complexes.

Accurate and internationally traceable radionuclide standards are imperative for the sale and export of radioactivity, ensuring that patients are treated with the intended doses in nuclear medicine, monitoring of radioactive pollution, nuclear science research, etc. South Africa has a relatively strong nuclear industry with the main contributors being NECSA, iThemba LABS, Koeberg nuclear power station and the many nuclear medicine facilities, all of which require radionuclide standards for their daily operation.

For a national metrology laboratory to prepare internationally recognised standards, it needs to demonstrate equivalence of its activity measurements to other national laboratories. Section II of the Consultative Committee for Ionizing Radiation (CCRI(II)) of the International Committee of Weights and Measures (CIPM) enables laboratories to do this by organising comparisons of the activity measurements of a given radionuclide solution. Alternatively, the International Reference System (SIR) maintained at the BIPM is available for a laboratory to demonstrate equivalence of an absolute standardisation with other laboratories at any time, but the system is only applicable to gamma-emitting radionuclides. The Extension of the SIR working group (ESIR WG) of the CCRI(II) was formed to develop an analogous scheme for non-gamma-emitting radionuclides, based on a liquid scintillation counting system. The practical implementation of such a system is still to be defined in detail, but a reference liquid scintillation cocktail is required for this purpose. The use of a commercial cocktail is not feasible since variability between different batches of the same cocktail cannot be excluded and the exact compositions are protected by patent-rights and not known to the users. This information is essential for the determination of the counting efficiency of the scintillation source. This project aimed to develop a reference liquid scintillation cocktail that could be used in the ESIR.

PRELIMINARY COCKTAIL DEVELOPMENT

The basic mechanism for the detection of a pure beta-emitting radionuclide by liquid scintillation counting is explained schematically in **figure 1**. A basic liquid scintillation cocktail¹ would generally consist of a scintillator dissolved in an organic solvent. The so-called scintillator solute is a material which emits a weak light flash or scintillation upon interaction with a certain quanta of radiation – the intensity of this scintillation being a function of the energy of the radiation deposited in the scintillator. The solvent, which plays an important part in the energy transfer sequence, is essential to the scintillation process. Additional reagents may be added to aid miscibility between a radioactive sample and a solvent-solute system, to improve the efficiency of the liquid scintillator and to enhance the stability of counting sources.

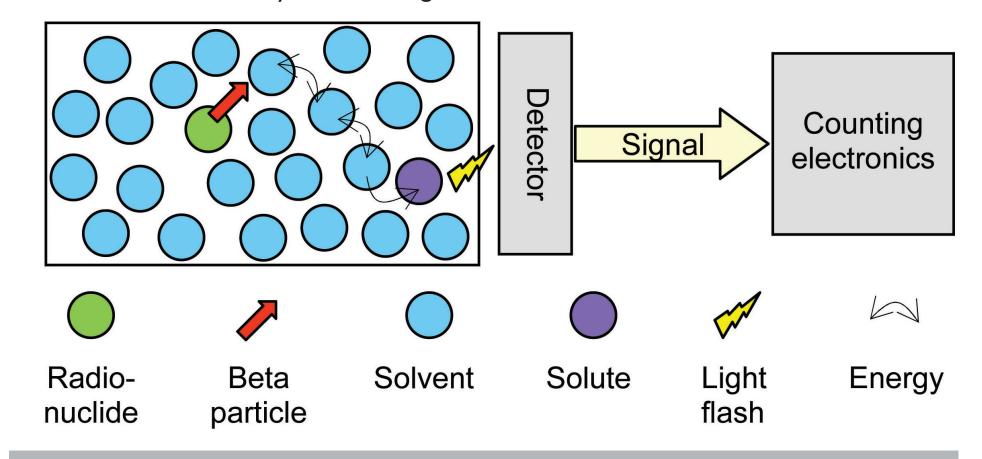


Figure 1: When a radionuclide dissolved in a liquid scintillation cocktail decays, the surrounding solvent molecules absorb a portion of the beta particle's energy. The energy passes between solvent molecules until the energy reaches the scintillator solute which absorbs the energy and re-emits it as light. The light is detected by a photomultiplier tube and a signal transmitted to the counting electronics.

the preliminary cocktails, nonylphenol 9 mole ethoxylate (Igepal CO-360) was added or used to substitute 2phenoxyethanol as an emulsifier to form liquid-liquid emulsion cocktails. In addition the complexing agent bis(2-

Testing of the preliminary cocktails was two-fold. Firstly, the abilities of the cocktails to form stable mixtures with the addition of 1 % acid were assessed by adding 100 μ l of 0.1 M HCl and 100 μ l 1.0 M HCl to separate 10 ml aliquots of the preliminary cocktails, shaking up and noting the physical appearances after 24 hours. Secondly, the ³H

ethylhexyl) phosphoric acid (HDEHP) was added to some of the cocktails as a chelating agent to bind radionuclides

2-phenoxyethanol

Figure 2: Chemical structures of the compounds used to prepare preliminary liquid scintillation cocktails.

Since p-xylene is known to be a good solvent for scintillator solutes and have excellent energy transfer properties¹ it was used as the primary solvent in the preparation of twelve cocktails for preliminary testing (**figure 2**). 2-Phenoxyethanol was added to facilitate mixing between p-xylene and aqueous radionuclide solutions to form real solution liquid scintillation cocktails². The aromatic nature of this compound was expected to also aid in energy transfer. The widely used scintillator solutes 2,5-diphenyloxazole (PPO) and p-bis-(o-methylstyryl)benzene (bis-MSB) were used for most of the preliminary cocktails, with one cocktail making use of 2-(4biphenyl)-6-phenylbenzoxazole (PBBO) instead. For some of

counting efficiencies of sources prepared by adding 33 – 85 mg of tritiated water to 10 ml cocktail were compared with similar sources prepared using the commercial liquid scintillation cocktail Ultima Gold from Perkin Elmer. Three cocktails were identified for further testing after demonstrating the ability to form clear and stable solutions or emulsions with the addition of 1 % acid and giving ³H detection efficiencies not much lower than that obtained with Ultima Gold (XP 34.2%, XI 38.4% and XPI 38.6% compared to UG

41.1%).

TESTING OF THE FINAL COCKTAILS

The compositions of the three final liquid scintillation cocktails tested are given in terms of mass fractions (%) in table 1. Counting sources were prepared in 20 ml counting vials by adding aliquots of seven different radionuclide solutions (3H, 63Ni, 14C, 89Sr, 90Sr/90Y, 55Fe and 36Cl) to separate 10 ml samples of each of the final liquid scintillation cocktails and also the commercial cocktail Ultima Gold for comparison. For the 3 H sources, 50 μ l of 0.2 M HCl or $50 \,\mu$ l of 2 M HCl were added to the cocktail before the addition of tritiated water so as to give sources with HCl concentrations of approximately 0.1 or 1.0 molar. For all sources, the total volume of solution added was made up to a minimum of 100 μ l by adding 0.2 M HCl.

Table 1: The compositions of the three final liquid scintillation cocktails prepared, given in terms of mass fractions (%).

	XP	XI	XPI
p-Xylene	49.49	49.54	67.38
2-phenoxyethanol	49.67		22.83
Igepal		49.69	8.99
PPO	0.80	0.70	0.74
bis-MSB	0.05	0.07	0.06

All sources were counted using a WALLAC automatic liquid scintillation analyser one to three days after preparation and recounted at intervals of about one week for three weeks. Each measurement consisted of a single acquisition of 600 seconds. Blank sources containing only 10 ml liquid scintillation cocktail were counted for the same time and the measurements used to correct for background.

To get an indication of the stabilities of the respective sources, the count-rates per unit mass were compared for repeat measurements of each source and the results displayed in figure 3. The maximum deviations observed for the widely used commercial cocktail Ultima Gold were less than 1.0 % for all sources except for 55Fe where the maximum deviation was 2.4 %. These deviations can be accounted for mainly by counting statistics. The XP sources showed similar repeatability, except for the strontium-based sources which showed a marked decrease in the count-rate over time (max deviation $^{89}Sr = 3.2 \%$ over two weeks, $^{90}Sr/^{90}Y$ 17.5 % over four weeks). The other two cocktails (XI, XPI) gave results that were somewhat worse, with stable sources obtained only for ³H, ¹⁴C and ³⁶Cl. The instability of the sources was caused by adsorption of radioactivity to the walls of the counting cells, leading to decreasing detection efficiencies.

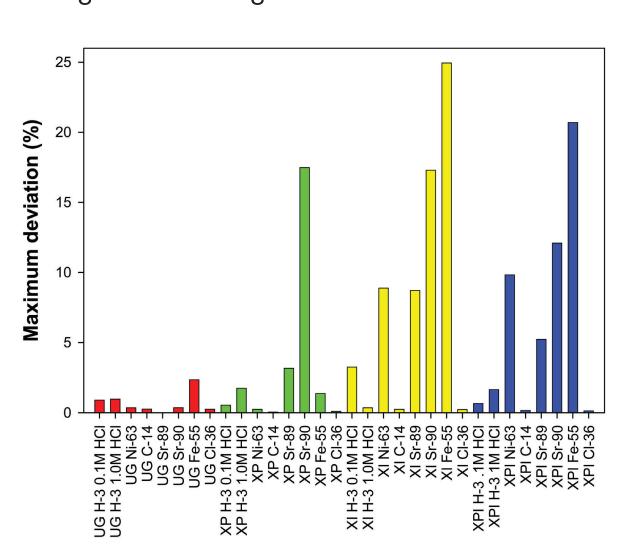


Figure 3: Maximum deviations observed between repeat measurements of the same source, displayed in red for Ultima Gold, green for XP, yellow for XI and blue for XPI.

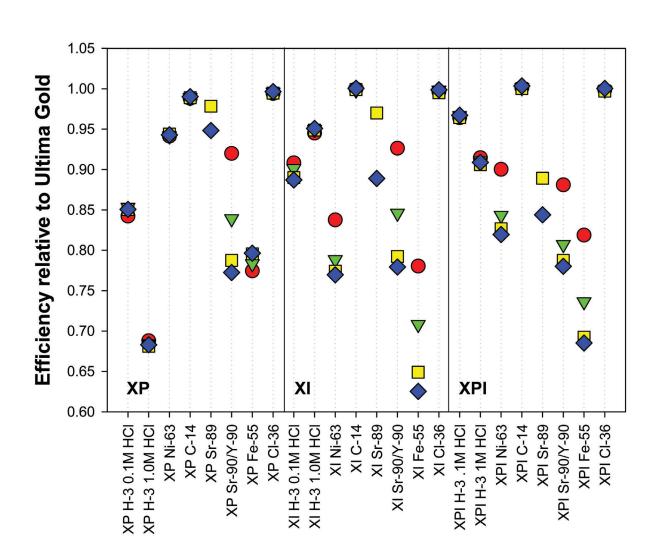


Figure 4: The counting efficiencies of the cocktails XP, XI and XPI relative to Ultima Gold are indicated by red circles shortly after source preparation, green triangles after one week, yellow squares after two weeks and blue diamonds after three weeks.

To get an indication of the detection efficiencies of the respective solutions, the count rate per unit mass of each source was compared with the equivalent Ultima Gold source and the relative efficiencies displayed in figure 4. The ³H efficiencies were somewhat lower than those obtained with Ultima Gold, but agreed with the efficiencies predicted by the preliminary test cocktails except for the XP source containing 1 M HCl. The particularly low efficiency of this source is possibly due to a problem with source preparation and should be investigated further. For the XP cocktail, good efficiencies compared to Ultima Gold were obtained for ⁶³Ni, ¹⁴C, ³⁶Cl with sources also being stable over time. The low-energy electron-capture radionuclide 55Fe gave a somewhat worse efficiency, but the counting source was stable. The two strontium-based sources 89Sr and 90Sr/90Y gave unstable sources which showed a decline in efficiency due to adsorption. Sources prepared with the other two test cocktails gave similar results except for those prepared with ⁶³Ni and ⁵⁵Fe which showed a decrease in efficiency over time due to instability of the sources.

CONCLUSIONS

Of the three final cocktails tested, the one based on the solvents p-xylene and 2-phenoxyethanol showed the most promise, fulfilling most of the requirements set out by the ESIR WG. The cocktail has a simple, accurately reproducible composition and makes use of chemicals that are readily available in a high chemical purity. Counting sources were stable for up to three weeks for most of the radionuclides tested and in various chemical matrices. The counting efficiencies obtained were reasonable, although not as high as with Ultima Gold for the lower energy radionuclides. The efficiencies could be improved by increasing the p-xylene/2-phenoxyethanol ratio but this has to be balanced with an increased tendency for adsorption. Further work is required to assess the ability of the XP cocktail to measure a more comprehensive list of radionuclides. Also, the intention is to develop variations of XP for those radionuclides giving unstable sources, for example by the addition of a complexing agent for strontium.

Once the ESIR is established and working, it will offer a means of checking measurements of pure beta emitters such as ³⁵S, ³³P, ³²P and ⁹⁰Y made for NTP Radioisotopes, a subsidiary of NECSA, and improve the international traceability of non-gamma-emitting radioactivity standards.

REFERENCES

- 1. Dyer A. (1980). Liquid scintillation counting practice (Heyden, London), p. 4-14, 30.
- Kellog T.F. (1983). Progress in the development of water-miscible non-hazardous liquid scintillation solvents. In: Advances in liquid scintillation counting, eds. McQuarrie S.A., Ediss C., Wiebe L.I. (Advances in liquid scintillation counting, Alberta), p. 387-393.

ACKNOWLEDGEMENTS

This work was performed at the LNHB in Saclay, France. One author (FvW) wishes to thank the South African Department of Science and Technology for funding.