

The Liquid Scintillation Counting of Iron-55 Using 'Aquasol'

G. A. Sutton and B. R. Harvey

Ministry of Agriculture, Fisheries and Food, Fisheries Radiobiological Laboratory, Lowestoft, Suffolk, England

INTRODUCTION

The work of monitoring and control of radioactive waste disposal to the marine environment, which is the primary responsibility of the Fisheries Radiobiological Laboratory (FRL), involves the detection and assay of numerous artificially produced radionuclides, often at very low levels. Determination is required in a wide variety of environmental materials including water, sediments and biota.

Although Iron-55 appears in the marine environment as a result of discharges of low-level radioactive waste from nuclear power stations, its greatest impact to date has been due to fallout from nuclear weapons testing; for instance, a study of the distribution of Iron-55 in commercial fish species of the North Atlantic by Preston¹ showed levels of $10\text{--}10^2$ pCi Iron-55/mg Iron.

In the past, two methods have been used at FRL to count these low-level samples for Iron-55; in both cases preliminary sample preparation involved wet ashing, followed by solvent extraction or ion-exchange chromatography to isolate iron. In one method the iron was electroplated on to a 2.5 cm copper disc and counted using a boron trifluoride proportional counter. Although this method provides an extra stage of decontamination from other radionuclides, the counting efficiency is rather low, even for a thin source (5 mg), and falls rapidly as the source thickness is increased. The other method was that of Eakins and Brown,² iron was precipitated as ferric hydroxide, dissolved in a minimum quantity of phosphoric acid and subsequently re-precipitated as the white ammonium ferri-phosphate which, when dispersed in gel scintillant, may be counted in a liquid scintillation spectrometer.

In the present method ferric hydroxide is dissolved in phosphoric acid, which is then incorporated directly into the liquid scintillation cocktail 'Aquasol'; considerable quantities of stable iron can be accommodated with little loss of counting efficiency, thus allowing samples of lower specific activity to be measured than would be possible with other methods. This is of considerable importance when analysing environmental samples in which the specific activity is often low.

EXPERIMENTAL

Preliminary sample treatment

Three essential factors must be considered when preparing samples for liquid scintillation assay of low specific activity Iron-55 :

1. Contamination from other radionuclides must be reduced to a very low level.
2. Stable iron contamination in processing chemicals must be reduced to a minimum and determined by running blanks.
3. Quenching, which may be caused by the constituents of the final iron solution.

When analysing animal tissue these factors, and particularly the second, are most readily controlled by using blood as the source of iron. Fish blood is drained into polyethylene bottles immediately after the fish have been caught; it is then stored at -20°C until required for processing. After thawing, the blood is homogenised in a liquidiser and sub-sampled as required for replicate determinations. 100 ml of blood containing up to 10 mg of iron (more if necessary) is wet-ashed with 50 ml of high purity (Aristar) nitric acid and then 100 ml of an equal mixture of nitric and perchloric acids. The dry residue from this ashing is dissolved in 50 ml of 0.5M HCl buffered to pH 6 with sodium acetate/ammonia solution and the heavy metal complex of iron with diethyl ammonium-diethyl-dithiocarbamate (DDDC) extracted into chloroform. Extraction using 10% DDDC in chloroform is repeated until the organic phase no longer becomes coloured on shaking with the sample solution. The organic layer is evaporated to dryness under an infra-red lamp and the organic residue destroyed by evaporating with concentrated nitric acid and 30% hydrogen peroxide. The final residue — which is white — is evaporated with concentrated hydrochloric acid to remove nitric acid residues, taken up in 5 ml of 2.5M HCl and applied to the top of a 10 ml column of Bio-Rad AG1 x 10 anion-exchange resin (30 cm long) previously conditioned with 2.5M HCl. The column is then washed with 2 bed volumes of 2.5M HCl and the iron fraction is subsequently eluted with 3.5 bed volumes of 0.5M HCl. The stable iron content of this fraction is determined spectrophotometrically. The stable iron blank must be determined repeating the whole process with the reagents only.

A suitable aliquot (e.g. 20 ml) containing a known amount of stable iron is then transferred to a counting vial in which ferric hydroxide is precipitated by the addition of concentrated ammonia (e.g. 3 ml). After centrifuging, the supernate is discarded, the precipitate being taken up in the given quantity of phosphoric acid needed to dissolve it completely.

Selection of optimum sample composition

Samples are prepared by the addition of suitable quantities of Aquasol and water to the solution of iron in phosphoric acid (see Appendix).

In order to achieve optimum counting efficiencies over a wide range of values of stable iron it was found that the relative proportions of water and phosphoric acid had to be varied.

Optimum water content for different amounts of stable iron. Two sets of samples each containing 5 mg of stable iron and the same amount of Iron-55 were prepared (see Appendix), containing 1.6 and 1.4 g of phosphoric acid respectively. 15 g of Aquasol were then added to all samples and varying amounts of water were added to each so that two series of samples were produced, each having a slightly different physical appearance. The counting efficiencies were determined and the results are shown in Fig. 1 (a) and (b).

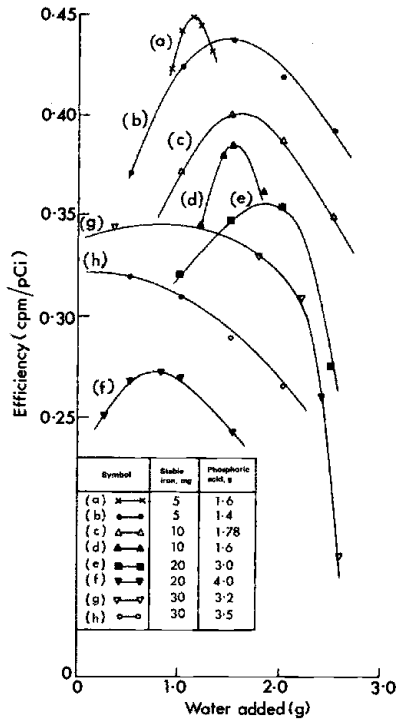


Fig. 1. Variation of counting efficiencies with the water added for various stable iron contents dissolved in a constant amount of phosphoric acid

Further sets of samples were then prepared in the same manner, to determine counting efficiencies for different amounts of stable iron (Fig. 1 (c-h)).

The effect of phosphoric acid. Figure 1 also shows that the phosphoric acid had a marked effect on the counting efficiency. This effect decreases as the amount of stable iron increases, and although the maximum counting efficiency is lower at higher levels of stable iron it is maintained over a much wider range of compositions.

Formation of three-component phase diagrams. The physical characteristics of the counting solution vary with increasing aqueous content, ranging from a clear liquid to a stiff gel. Between these two extremes there is a narrow range in which a two-phase system occurs.

As a starting point for producing the three-component phase diagrams it was assumed that maximum counting efficiency would occur with a clear, colourless sample; this was found to be the case. Figure 2 is a diagrammatic representation of how the counting efficiency varies with phosphoric acid/water content for samples containing 5, 10, 20 and 30 mg of stable iron. The phosphoric acid and water values are plotted along the two axes and the counting efficiencies shown by contours. These contours are formed by drawing a line through samples having the same counting efficiency.

For a sample containing 5 mg of stable iron, the optimum counting efficiency occurs over a very narrow range of phosphoric acid/water values. Slight variations in the amount of either reagent will produce a relatively rapid decrease in the

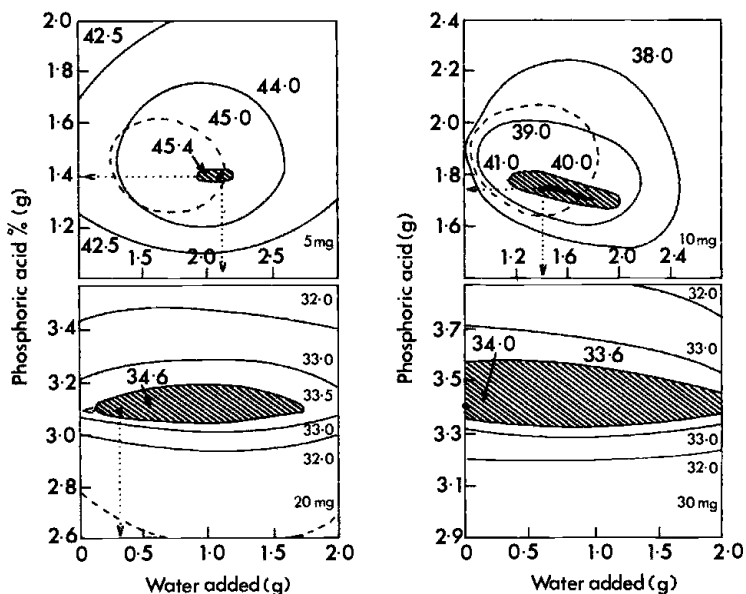


Fig. 2. Diagrammatic representation of the variation of counting efficiency with phosphoric acid and water content. Contours represent efficiency. Broken contours represent single/double phase boundary.

counting efficiency. As the stable iron content of the samples is increased, it is found that the phosphoric acid/water ratio becomes less critical, and variation of either reagent will not produce such a large decrease in the counting efficiency.

Weight for weight, the phosphoric acid has a greater ability to cause gelling of the Aquasol than has water. For low stable iron contents, where the optimum counting efficiency is at a critical position, addition of phosphoric acid to the samples provides a coarse adjustment of the physical characteristics of the sample. Water added drop by drop thus enables the critical position for optimisation to be achieved. As the stable iron content increases, the need for fine adjustment of the physical characteristics of the sample becomes unnecessary because the optimum conditions become less critical, and optimisation can be achieved by using a larger proportion of phosphoric acid.

Characteristics of the final counting solution

Colour and viscosity. By increasing the phosphoric acid content of a sample containing a constant amount of stable iron, the appearance of the final counting solution is changed from a thin cloudy solution, through a clear phase, which gives good counting efficiencies, to a semi-viscous cloudy solution which gives relatively poor counting efficiencies. The viscosity of the solution varies with the stable iron content, i.e. for 5 mg of stable iron the appearance of the solution giving optimum counting efficiency was that of a clear thin solution, whilst for 30 mg of stable iron it was a clear viscous gel. Similar results are obtained by varying the water content, keeping stable iron and phosphoric acid constant.

When in slight excess, phosphoric acid produces gelling and enhances the counting efficiency of the final solution. However, too much phosphoric acid produces a green, apparently insoluble, solid which renders the sample unsuitable for assay.

Formation of two phases. It was found that certain samples suffered from phase separation whilst in the refrigeration compartment of the spectrometer. These samples are indicated by broken contours on Fig. 2. In such samples the problem is resolved by adding a further small quantity of water, which produces a more viscous single phase solution without any serious decrease in the counting efficiency.

Variation of count rate and counting efficiencies with stable iron content

Figure 3 (a) shows the maximum counting efficiencies obtained in these experiments for various amounts of stable iron. The quantities of phosphoric acid and water which produced these maxima are plotted in Fig. 3 (b); for example, for 5 mg of stable iron the sample contained 1.4 g of phosphoric acid and 2.3 g of water, giving an efficiency of 43.4%. From these graphs the operator may select the optimum composition for any sample. At the low stable iron values, maximum counting efficiencies are higher because water has a lower quenching effect than phosphoric acid.

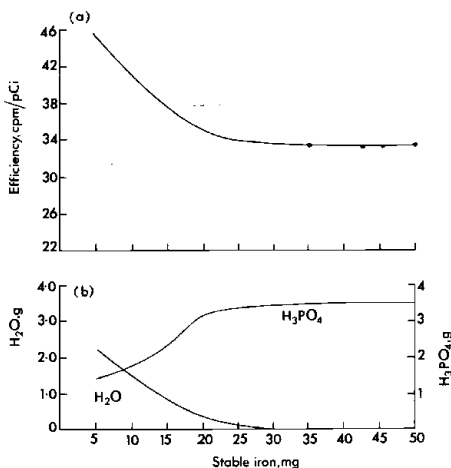


Fig. 3. Optimum sample composition.

COMMENT

The specific activity of environmental samples is often very low and consequently it is desirable to be able to prepare samples for counting which give the maximum counter response. Figure 4 compares the counter response versus stable iron content obtained by the present method and that of Eakins and Brown. It can be seen that for the present method a maximum has not been reached at 50 mg of stable iron; however, this is almost the practical limit for stable iron set by the quantities of reagents needed, relative to the volume of the vials.

Where the amount of stable iron in a sample is, for other reasons, limited to less than 10 mg, the method of gel scintillation (curve b, Fig. 4) offers the advantage of a lower background (about 5 c.p.m.) and slightly higher efficiency. However, where the specific activity is low and sample size is not a limiting factor, then the present method (curve a, Fig. 4) offers considerable advantages even with a higher background (about 10 c.p.m.)

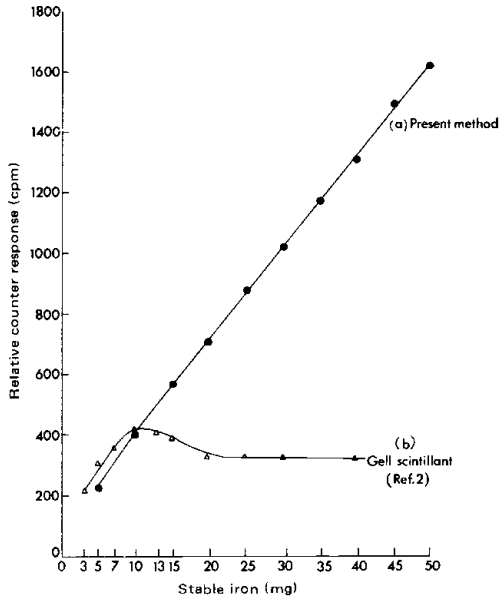


Fig.4. Variation of counter response with weight of stable iron.

REFERENCES

- 1 A. Preston, Marine Biology 6 (4), 345-9 (1970).
- 2 J.D. Eakins and D.A. Brown, United Kingdom Atomic Energy Research Establishment Report No. R4946, 1965.
- 3 R. Loevinger, M. Berman, Nucleonics 9 (1), 26-39 (1951).

APPENDIX: SELECTION OF OPTIMUM COUNTING CONDITIONS (USING A PACKARD TRICARB MODEL 3320)

Gain

With the upper discriminator set at 1000, and the lower at 50 (i.e. full window), a sample was counted at various gain settings (0-100 %). A graph of counts per minute against gain settings was then plotted (Fig. 5).

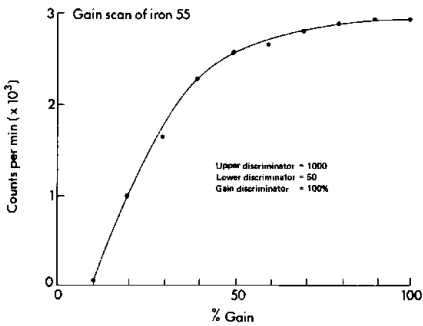


Fig. 5. Selection of optimum gain.

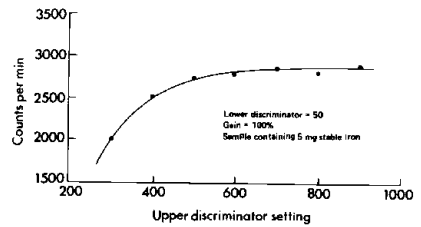


Fig. 6. Selection of optimum upper discriminator setting.

It was found that the maximum count-rate was obtained at a gain setting of 100% i. e. optimum gain setting for the counting of Iron-55 was 100%.

Upper discriminator

With the gain set at 100% and the lower discriminator at 50, a sample was counted for various upper discriminator settings. A graph of count-rate against upper window settings was plotted (Fig. 6). It can be seen from Fig. 6 that the count-rate increases relative to the upper discriminator settings, and reaches a maximum at 1000. However, an upper setting of 1000 is not necessarily the optimum setting, because the count-rate for a sample blank may also increase.

Lower discriminator (Fig. 7)

With the upper discriminator set at 1000 and the gain at 100%, a sample was counted for various lower discriminator settings (0-400). It was found that, for 100% gain, the count-rate increases as the lower discriminator setting is decreased. However,

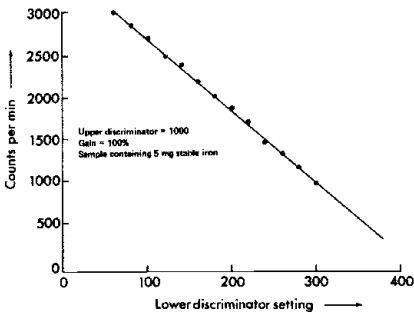


Fig. 7. Selection of optimum discriminator settings for the counting of ^{55}Fe .

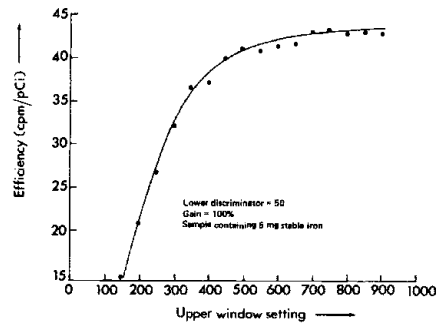


Fig. 8. Variation of efficiency with upper window setting.

the optimum lower setting was not chosen as zero, but 50, in order to maintain a high count-rate while keeping the background interference to a minimum. Thus, for the counting of Iron-55, a lower discriminator setting of 50 was chosen.

Figure of merit (E^2/B)

The ratio E^2/B (where E^2/B = counter sensitivity in counts per unit time per unit of activity) is often taken as a figure of merit criterion for optimization;³ strictly it applies to conditions when the sample count-rate is small relative to the background. Under more favourable circumstances the sensitivity (efficiency) alone may be the most suitable criterion. Thus both criteria must be considered in the optimisation of a system required to measure a wide range of sample strengths, though for the purposes of this work the system has been optimised for maximum E^2/B .

Both E^2/B and efficiency vary with upper discriminator settings (Figs. 8 and 9). It was found that a maximum occurs for E^2/B between 300 and 350 (upper levels), but there was only a small decrease in counting efficiency if the upper window was lowered from 1000 to 500.

Since the values of the upper discriminator for the optimisation of E^2/B and counting efficiency were not the same, a compromise was made, and an upper discriminator setting of 450 was chosen.

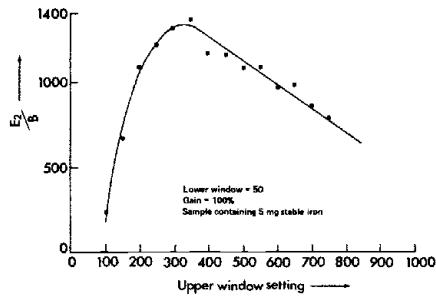


Fig. 9. Variation of E^2/B with upper window setting.

Summary of optimum counting conditions

Gain	=	100 %
Upper discriminator	=	450
Lower discriminator	=	50

DISCUSSION

J.D. Eakins: Was the difficulty you experienced in suspending the ferriphosphate complex only with 20 mg samples or did you have troubles with lesser amounts as well?

G.A. Sutton: The main problem turned out to be due to a poor batch of gel scintillator. With good materials we had little difficulty with samples in the 5–8 mg range, but settling out did occur at levels of 20 mg or more.