

Chapter 9

Methods of Sample Preparation of Inorganic Materials including Cerenkov Counting

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INTRODUCTION

This review will concern itself with the radiochemical determination of inorganic isotopes by liquid scintillation counting. It will include cases where the isotopes are recovered as inorganic materials from biological materials. The recovery of calcium-45 as calcium chloride, from milk, and that of iron isotopes, as ferric chloride, from blood are two examples of this general technique.

Some fifty isotopes have been estimated by liquid scintillation counting or closely related procedures. The use is not confined solely to methods whereby a scintillator solute-solvent system is activated by a β -particle. The references cited herein include the determination of γ , β^+ , α and electron capture isotopes as well as cases where a liquid scintillation spectrometer is used to record photons from Cerenkov radiation and plastic scintillators.

The advantages of using liquid scintillation methods over the more traditional methods of counting inorganic isotopes can be summarized as follows:

1. speed and reproducibility of sample preparation;
2. the counting geometry tends to maximize counting efficiency when dealing with (i) low activity samples, (ii) low energy emitters;
3. convenient method for small volumes of solution;
4. automatic nature of the modern equipment gives a gain in convenience and ease of data processing when large numbers of samples are to be monitored;
5. possibility of adaptation for flow cell use;
6. suitable for fundamental studies of nuclear processes and absolute counting.

FUNDAMENTAL STUDIES

As most of the earlier literature involves the use of liquid scintillation procedures for fundamental investigations a brief survey of this will be considered first.

Many workers have found it a useful method for absolute counting and related studies. Particularly well investigated are α -emitting isotopes as studied by Horrocks and his co-workers.⁵⁶ They have examined astatine-217, rhodium-220, thorium-232, uranium-233, uranium-236, plutonium-236, plutonium-238, plutonium-239 and curium-242. Similar

studies have been made by Basson⁴ on astatine-211, and by Joon and Deurloo,^{73,74} Flynn *et al.*³⁴ on plutonium-239. Stoicovici and Uray¹²⁸ also studied uranium isotopes.

Horrocks^{55,57} has also paid attention to the β -emitters, etc.; sulphur-35, iron-55, nickel-63, yttrium-90, ruthenium-106, cadmium-109/silver-109, tin-113/indium-113m, caesium-137/barium-137m, samarium-151, plutonium-241, californium-252. Analogous work on sodium-22, sodium-24, phosphorus-32, cobalt-60, iodine-131 and gold-198 has been done by Steyn,^{126,127} and on zirconium-95/niobium-95 by Ludwick.⁸⁷ Josefowicz⁷⁵ has also examined phosphorus-32.

Ryves¹¹³ has used samples deposited upon polymer film, which are then immersed in a PPO/POPOP in toluene scintillator, to obtain absolute counting efficiencies close to 100% for the isotopes sodium-24, phosphorus-32, cobalt-60, thallium-204.

Joon and Deurloo⁷⁴ commented on the stability of carrier-free solutions and recommended the use of tri-n-octyl phosphine oxide as a stabilizer when counting zirconium-95, ruthenium-106, cerium-144 and plutonium-239. Erdtmann²⁹ showed how similar problems may be overcome by additions of carrier or powdered silica.

Half-life studies of isotopes held in liquid scintillator solution are known for the isotopes nickel-63,⁵⁸ rubidium-87³⁵ and samarium-147.¹⁴² Horrocks^{60,61} has examined pulse height energy relationships for electrons and photoelectrons in liquid scintillation media for strontium-85, cadmium-109/silver-109, tin-113/indium-113m, indium-114, barium-133, caesium-137/barium-137m, mercury-203, astatine-217/thorium-229, thorium-232, uranium-233, americium-241 and curium-242. Similar studies by Flynn³⁴ (plutonium-239) and by Seliger¹²¹ (phosphorus-32, caesium-137/barium-137m, polonium-210) may also be noted.

All of these investigations necessitate the incorporation of the inorganic isotope into mutual solution with a scintillation medium and often form the basis for routine sample preparation. This aspect of these fundamental studies is covered in the subsequent text.

PRACTICAL ASPECTS

Isotopes can be incorporated into phosphors as solids, liquids or gases.

Solid samples

Generally the solid is dispersed, usually as a fine powder, in the scintillator medium. The methods of dispersion can be summarized.

Use of a gelling agent. This has been used by Yarbrough *et al.*¹⁴⁴ to estimate calcium-45 and strontium-89 in unicellular algae. The algae are dehydrated, decolorized and then dispersed, in a PPO/DMPOPOP in toluene scintillator, by Cab-O-Sil. Turpin and Bethune¹³⁶ used the same suspension agent for calcium-45 containing solids obtained from urine and plasma, whereas Ott *et al.*¹⁰⁰ evolved a similar method for strontium-89 in bone ash. (Note also Scales and McIntosh).¹¹⁷

The isotopes iron-55 and iron-59 can be counted in a like manner. Eakins and Brown²⁶ suggest a suspension of a ferriphosphate complex, whereas Graber *et al.*⁴⁴ use a ferric benzene phosphinate. (See also Katz *et al.*)⁷⁶

An earlier gelling agent was Thixcin (a castor-oil derivative) which White and Helf^{51,141} used with a PPO in toluene scintillator for sodium-22, chlorine-36, nickel-63, strontium-90/yttrium-90, barium-133 and lead-210 as simple salts.

Fleishman *et al.*^{33,122} report the use of a methyl methacrylate gel, formed by warm-

ing together the labelled solid, polymer and a *p*-terphenyl/POPOP in toluene phosphor. They claim 100% efficiency for potassium-40, strontium-90 and caesium-137. Recently Benakis⁶ proposed a similar gel of polyolefinic character, used with both PPO/POPOP and butyl PBD/POPOP, to estimate inorganic samples. Materials estimated were calcium-45, strontium-90 as sulphates, iron-55 and iron-59 as ferriphosphate or ferric benzene phosphinate complexes, caesium-137 as perchlorate and iodine-131 as sodium iodide. (N.B. Ihle⁶⁸ has used a PVC-acetate copolymer for α -emitter estimations).

Use of glass fibre filter paper. Johnson and Smith⁷¹ deposited barium sulphate containing sulphur-35 on glass fibre filter paper, homogenized it in a naphthalene/PPO/POPOP in dioxane scintillator, and claimed a convenient and efficient method. Lerch and Cosandey⁸³ counted phosphorus-32 and calcium-45 as calcium phosphate in a similar manner. Hutchinson⁶⁷ preferred calcium chloride deposition (for calcium-45) when dealing with urine, plasma, stool digests, and tissue extracts. He used a PPO/POPOP in toluene scintillator. Cramer and Ross¹⁸ ashed biological tissue and bone containing calcium-45 and compared cellulose to glass fibre papers (as well as other methods). They found cellulose paper superior as it is not prone to shed lint, although glass fibre paper was the most efficient. Fairman and Sedlet³¹ have used an anion exchange paper dispersion to determine technetium-99.

Simple mixing. Dyer *et al.*²⁴ have counted iron ore, containing sodium-22, by placing it in a scintillator and have found this simple method as successful as chemical extraction of the sodium-22 as sodium chloride followed by incorporation into a Hayes and Gould solution, or, directly G-M counting the ore. Nisson and Benson⁹⁸ used this simple approach, with a Bray scintillator, for plant roots containing potassium-42.

Liquid samples

Use of a labelled compound soluble in a scintillator solvent. The ideal counting conditions would be to produce an inorganic material of sufficient solubility in a scintillator solvent. The nearest approach to this is the use of PBD in toluene to take up chlorine-36 in the form of silicon tetrachloride. This was the method of Ronzani and Tamers¹¹¹ as a dating technique for sodium chloride in ground waters.

Use of aqueous solutions of inorganic salts. This again is a simple method, a blending solvent being used to form a homogeneous sample in a 'cocktail'. There are several techniques described for the counting of calcium-45 in this way. Samples of biological origin (serum, urine, bone, blood and milk) are variously treated to yield a precipitate of calcium oxalate which is then dissolved in aqueous mineral acid and blended with ethanol in a toluene-based phosphor. Methods of this type are due to Carr and Parsons,¹⁴ Sarnat and Jeffay,¹¹⁵ Vemmer and Guette,¹³⁹ and Kumar.⁸⁰

Similar methods are available for iron-55 and iron-59 from Dern and Hart,²¹ Jenner and Obrink⁷⁰ and Perry and Warner.¹⁰⁵ The iron is as chloride or perchlorate and ascorbic acid may be added as a stabilizer.

Dyer *et al.*²³ have given counting conditions for sodium-22, silver-110m, promethium-147 and thallium-204 whereby aqueous salt solutions are taken into a Hayes and Gould type cocktail. (Note also Klumpar and Majerova⁷⁸ for calcium-45, strontium-90/yttrium-90 and thallium-204).

Plutonium isotopes, from biological sources, have been estimated in this way by Toribara *et al.*^{133,134} as chlorides and by Lindenbaum and Lund⁸⁶ as nitrates.

Table 1. Use of complexing agents.

Isotopes	Cocktail	Experimental details	Comments	Reference No.
Iron-59	PPO/POPOP (Hayes and Gould)	Iron- <i>ortho</i> -phenanthroline complex, 50% efficiency	Iron metabolism studies	82
Iron-55	DMPOPOP/PPO/ naphthalene/toluene	Iron-di(2-ethyl hexyl phosphoric acid) (HDEHP) complex	Blood	17
Nickel-63	NE 240	[NiPy ₄] (CNS) ₂ complex	Effluent from AGR reactors	48
Plutonium-249, Americium-241	PPO/POPOP/ naphthalene/dioxane	Tri-n-octyl phosphine oxide (TOPO) complex	Comparison with other methods	68
Plutonium-249	<i>p</i> -terphenyl/POPOP/ toluene	Acid extraction from ashed samples by HDEHP	Biological samples	77
Plutonium-241, nickel-63, samarium-151, sulphur-35, ruthenium-106/rhodium-106	<i>p</i> -terphenyl/POPOP/ xylene	Sm, Pu as HDEHP in HCl, nickel-63 as di-octyl phosphate complex, sulphur as Na ₂ SO ₄ , Ru/Rh <i>p</i> -toluidine complex	Absolute disintegration studies	55
Plutonium-239, curium-242, thorium-232, uranium-233, astatine-217, californium-252, yttrium-90	DMPOPOP/PPO/ toluene	HDEHP extraction in xylene. Quenching studied	α -resolution studies, etc.	56, 57
Plutonium-239, ruthenium-106, cerium-144, zirconium-95, uranium	DMPOPOP/PPO/ naphthalene/dioxane	TOPO - carrier free, comments on stability		74
Cerium-144, cobalt-60, sodium-22	POPOP/PPO/naphthalene/ dioxane/xylol/ethanol	HDEHP complexes	Counting loss studies	29
Promethium-147	DMPOPOP/PPO	HDEHP complex	Urine assay	88
Promethium-147	POPOP/PPO/naphthalene/ dioxane	HDEHP in 0.1 M HNO ₃	Fission products	9

Table 1. Use of complexing agents (contd.).

Americium-241, curium-244, europium-152	PPO/POPOP	HDEHP complex from aqueous oxalate and sulphate solution at pH 3.6 and constant ionic strength	Ion-exchange effluent	3
Thorium-232, nickel-63, cadmium-109, barium-133, americium-241, samarium-113, indium-113m, mercury-203	<i>p</i> -terphenyl/POPOP/ xylene DMPOPOP/PPO/toluene	HDEHP complexes	Half-life and other fundamental studies	56,61
Thorium-232	<i>p</i> -terphenyl/POPOP/ toluene	DOP complex		41

Table 2. Use of metal organic salts.

Isotopes	Cocktail	Experimental details	Comments	Reference No.
Caesium-137/barium-137m	DMPOPOP/PPO/ toluene	Salt of 2-ethyl-hexanoic acid (octoate)		60
Rubidium-87	<i>p</i> -terphenyl/POPOP/ toluene	Octoate	Half-life studies	35
Calcium-45	PPO/POPOP/toluene + ethanol	Octoate from oxalate in HCl	Biological fluids	89
Strontium-90/yttrium-90	PPO/POPOP/toluene	Octoate	Assays	138
Mercury, cadmium, calcium, potassium, rubidium		Metal loaded scintillators using octoates		20, 112
Samarium-147	<i>p</i> -terphenyl/POPOP/ toluene	Octoate	Half-life studies	142
Plutonium-239		Octoate		34
Nickel-63	PPO/POPOP/toluene + ethanol	<i>n</i> -caproate		40

Table 3. Complexing or extraction with emulsifier added.

Isotopes	Cocktail	Experimental details	Comments	Reference No.
Phosphorus-32	PPO/POPOP/toluene	Phosphomolybdic acid, extracted n-butanol/ethyl ether/ethanol. Add Hyamine 10-X	Food analysis	27
Calcium-45		Add Triton X-100	Urine and serum	96
Calcium-45, iron-55, rubidium-87, samarium-147, strontium-90, strontium-89, chlorine-36	PPO/bis MSB/xylene	Ca, Fe as fluoride, Rb, Cl, Sr, Y as chloride, Pm co-precipitated as oxalate with praeosdymium, then as EDTA complex. All with Triton N-101 added.	Low-level counting	92
Iron-55, Iron-59	PPO/POPOP/toluene	Ferrous citrate + Hyamine 10-X	Plasma samples	91
Chromium-51, manganese-54, iron-55, zinc-65, yttrium-88, iodine-125	PBD or PPO/POPOP/toluene/ethanol	Cr as chloride or chromate, Mn as nitrate, Fe, Zn, Y as chloride, I as potassium iodide, Triton X-100 added	Electron capture nuclides	130
Cobalt-60	BBOT/toluene	Co ^{II} thiocyanato complex with Triton X-100	Low-level counting of environmental waters	15
Chromium-51		Cr as EDTA complex. Triton X-100 added	Simultaneous measurement with carbon-14.	123

Table 4. Solvent extraction procedures.

Isotopes	Cocktail	Experimental details	Comments	Reference No.
Calcium-45	PPO/toluene	Calcium perchlorate extracted by tributyl phosphate (TBP)	Biological sources	66
Calcium-45	PPO/ α -NPO/toluene <i>p</i> -terphenyl/ α -NPO/	Calcium chloride extracted by dibutyl phosphate (DBP). Quenching studies	Agricultural materials, plants and soils, etc.	47
Strontium-90/yttrium-90		DBP extraction		36
Plutonium-241	<i>p</i> -terphenyl/POPOP/ xylene	DBP extraction from 1 M HCl		54
Yttrium-90, plutonium		TBP extraction	Agricultural materials	99
Americium-241, uranium-233	DMPOPOP/PPO/ naphthalene/dioxane or BBOT/toluene	Tri-isocetylamine + 30% DMF extraction		120
Thorium, uranium	<i>p</i> -terphenyl/ α -NPO/ toluene	TBP extraction		2, 30

Low levels of uranium have been counted by Levin⁸⁴ in aqueous solutions blended in a dimethoxyethane/naphthalene/PPO/POPOP cocktail. Other authors mention similar determinations of manganese-56,²² bismuth-210³² and polonium-210.³²

Absolute standardization studies, as mentioned earlier, often use related procedures. Seliger¹²¹ incorporated cobalt-60, caesium-137/barium-137m, gold-198 and polonium-210 as chlorides and Steyn^{126,127} mentioned the use of sodium-22, sodium-24 as acetate, phosphorus-32 as phosphoric acid and iodine-131 as sodium iodide. Ludwick⁸⁷ used a Davidson and Feigelson²⁰ cocktail for niobium-95/zirconium-95 estimation.

Use of complexing or solubilizing agents. These methods depend upon the use of an organic material to produce a complex, or ion-association complex, of a metal isotope which then has an appropriate scintillator solvent solubility. Obviously a colourless end-product is advisable, and hence phosphate complexing agents have been used widely. Nevertheless, at least two viable methods using coloured complexes are reported. Harvey and Sutton⁴⁸ used the pale blue tetrapyrindino nickel-63^{II} thiocyanate and Leffingwell *et al.*,⁸² the red iron-59 *ortho*-phenanthroline complex. A summary is given in Table 1.

Use of an organic salt of the metal isotope. Here a metal salt of an organic acid (e.g. an octoate) often has sufficient solubility in the alkylbenzenes to facilitate liquid scintillation counting. (See Table 2 for details).

Some authors have found it an advantage to add a further emulsifying and solubilizing agent to the counting mixtures or that a subsequent solvent extraction step is advisable. These instances are given in Tables 3 and 4.

Sulphur-35 determinations. Radin and Fried¹⁰⁸ converted ³⁵S-containing materials to sulphuric acid prior to counting as suspensions in Primene 81-R in a terphenyl/POPOP in toluene scintillator, whereas Lloyd and Rees-Evans⁸⁵ suggested conversion to lithium sulphate. Jeffay *et al.*⁶⁹ used a modified Piries reagent to convert biological material to magnesium sulphate; this is then extracted into a glycerol/ethanol/DMF mixture which is miscible with PPO/POPOP in toluene.

Gaseous samples

The application of the liquid scintillation technique for the estimation of radioactive gases depends upon two techniques:

1. 'trapping' the gas, i.e. stoichiometric conversion into a liquid or solid compatible with a scintillation mixture;
2. dependence upon the gas having a reproducible solubility in a scintillator solvent.

Trapping techniques have been used by Urone *et al.*,¹³⁷ whereby ³⁵SO₂ was taken into Na₂Hg₂Cl₄ or H₂O₂/H₂SO₄ solutions and counted in a DMPOPOP/PPO/naphthalene in dioxane mixture. (N.B. Rapkin²² has suggested that the use of ethanolamine as a trapping agent may be better). Mahadevappa and Eager⁹⁰ converted H₂³⁵S to Na₂S₂O₃ and Na₂S₄O₆ which was then trapped by hyamine hydroxide in a Hayes and Gould scintillator. Gordon *et al.*⁴³ used a similar method but concluded that it was better to rely on the dissolution of the gas in toluene contained in a serum-capped vial.

As the rare gases have appreciable solubilities in toluene, Horrocks and Studier⁵⁹ have been able to count krypton-85, xenon-131m and radon-222 in this way. (See also Curtis *et al.*,¹⁹ Schwendiman and Mishima,¹¹⁹ Moghissi,⁹² as well as Noguchi).⁹⁷ Note: These methods use a pre-evacuated counting vial, or ampoule, into which the gas and scintillant are injected (or pre-frozen). PPO and POPOP are the preferred phosphors.

Other methods

Use of a scintillating ion-exchange resin. Heimbuch⁵⁰ has developed a resin bead copolymerized with a phosphor (9,10-diphenylanthracene or *p*-terphenyl). This can be used for both anion and cation exchange, even in concentrated acid and alkali conditions. Such isotopes as sulphur-35, chlorine-36, nickel-63, strontium-90/yttrium-90, iodine-131, neptunium-237 and plutonium-239 were counted in this way.

Use of a suspended scintillator. Anthracene, of the blue-violet fluorescence grade, may be wetted by a Triton type detergent and suspended in an aqueous labelled sample. The method was developed by Steinberg,^{124,125} who used it for phosphorus-32, calcium-45 and iodine-131. Myers and Bush⁹⁵ used the technique for beryllium-7, H₃³²PO₄, H₂³⁵SO₄, strontium-90/yttrium-90, caesium-137 and polonium-210. They examined the effect on counting efficiency due to the presence of methyl and ethyl alcohols, acetic acid, and acetone.

Use of scintillator granules or shavings. Tsirlin *et al.*¹³⁵ counted aqueous salt solutions (sodium-22, potassium-40) by placing granules of anthracene in them. Sax *et al.*¹¹⁶ determined atmospheric krypton-85 in a gas-tight vial full of plastic scintillator shavings.

Flow cells. Continuous monitoring can be achieved by passing solutions of isotopes through either (a) a tube constructed of plastic scintillator, or (b) a vial containing rods or granules of scintillator. Schram¹¹⁸ recently has commented on this method, which has been used by Tkachuk¹³² (potassium-40, strontium-90/yttrium-90), Sanson and Taylor¹¹⁴ (phosphorus-32, calcium-45) and Pickering *et al.*¹⁰⁷ (calcium-45 in bone dissolved in 1 M nitric acid).

PROBLEMS AND GENERAL COMMENTS ON THE COUNTING OF INORGANIC MATERIALS

Solutes. It can be seen from previous details that PPO and POPOP are often compatible with inorganic sample determinations, but that *p*-terphenyl can often be a cheaper alternative. This should be remembered in designing scintillator systems for inorganic use provided that determinations are not to be carried out in a machine whose sample chamber is maintained at a low temperature which will cause *p*-terphenyl to come out of solution.

Solvents. Toluene, xylene and dioxane seem adequate in most cases. Recently, Gomez *et al.*⁴² have reported the use of benzo- and acetonitriles as scintillator solvents. They found them particularly useful for the dissolution of ferric, lithium, mercuric, antimony, and copper chlorides, and zinc acetate.

Vials. The use of siliconized vials may be useful to prevent adsorption of metallic isotopes onto the glass, as suggested by Petroff *et al.*¹⁰⁶

Temperature control. Horrocks⁶³ recently advised that a reasonable control of temperature was required in the counting of uranium-233 as DBP complex. This may well be a universally applicable comment.

Quenching and its correction. Obviously colour quenching can be a problem and chemical quenching can arise in the presence of acids, alkali, inorganic salts or complexing and blending agents. Forster³⁷ made a detailed study of the quenching arising in the counting of β -emissions from promethium-147. Blair and Murrenhoff⁷ also considered this specific problem, and Peng¹⁰⁴ has made some more general comments. Many of the authors quoted herein consider quenching problems which, of course, are more noticeable with the low β -energy of calcium-45 and the electron capture nuclides (e.g. iron-55). Generally it has

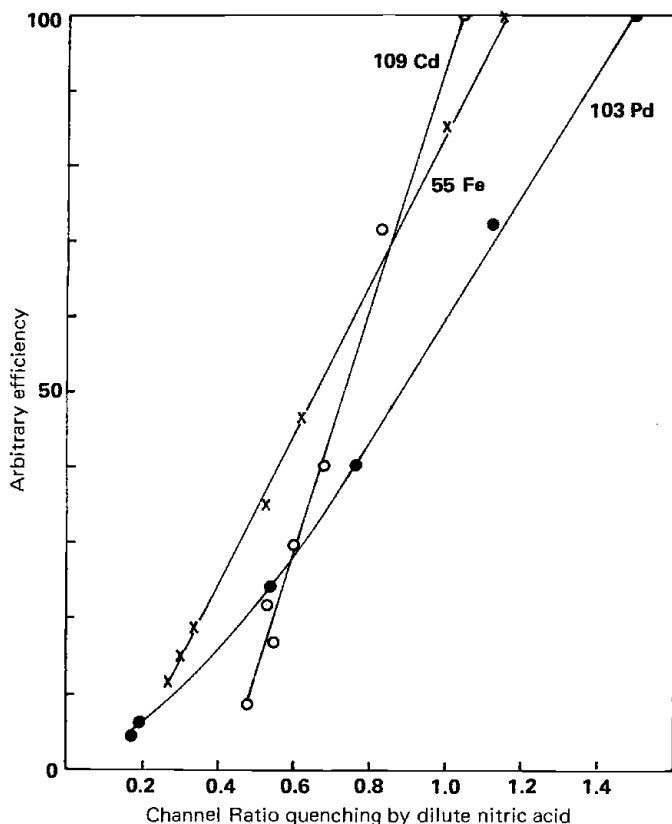


Fig. 1. Some examples of quench correction.

been concluded that the standard methods of quench correction, such as that of channels ratio, are applicable. Some examples²⁵ are given in Fig. 1.

Simultaneous counting of two or more isotopes. Yerick and Ross¹⁴⁵ as well as Rhodes¹⁰⁹ examined the simultaneous counting of the isotopes iodine-125, iodine-128, iodine-131. Zaduban¹⁴⁶ used an amplitude attenuation method to deal with iodine-131 in the presence of tritium and carbon-14. Muller,⁹⁴ in his studies of bone metabolism, designed a triple-tracer method for phosphorus-32, calcium-45, strontium-89. Double isotope studies have been carried out by Ludwick⁸⁸ (zirconium-95, niobium-95), by Hoyer⁶⁴ (iron-55, iron-59), and Katz *et al.*⁷⁶ (iron-55, iron-59).

Kobayashi and Maudsley⁷⁹ recommend the use of an Enberg plot to determine counting conditions for simultaneous estimations of two isotopes.

The iron isotopes. The counting of iron isotopes has received much attention in the recent literature and the general methods are listed in Table 1 or in the text. Practitioners should be aware of the comments on the reproducibility of iron-55 measurements in the presence of iron-59, which have been made by Hoyer.⁶⁴ Horrocks⁶² has suggested the possibility of maximizing iron-55 counting efficiency to 90% by including the K, L, M X-rays and Auger electrons, in addition to the 5.9 keV K-X manganese electrons normally counted.

Chemiluminescence. This can arise and we have noted its occurrence in counting zinc-65 and barium-133 in a Hayes and Gould system.

Comparative studies. Some authors have made detailed investigations of the liquid scintillation technique in comparison with other counting techniques for the counting of inorganic isotopes. These have been generally favourable and are summarized in Table 5.

CERENKOV COUNTING MAKING USE OF LIQUID SCINTILLATION EQUIPMENT

Introduction. In 1953 Belcher⁵ reported the detection of a faint luminescence from aqueous solutions of high energy β^- -emitters. He concluded that this was mainly due to Cerenkov radiation which arises as a blue-white light emitted by the interaction of β^- -particles of energy >300 keV with liquids such as water. Cerenkov radiation is thought to be the source of the sudden light flashes we all have experienced in our eyes. The light is in the near ultraviolet and is detectable by modern automatic liquid scintillation spectrometers designed to cope with very low intensity light pulses. The problems of detecting these weak emissions have been likened by Parker and Elrick¹⁰¹⁻¹⁰³ to those encountered in tritium counting and they have used tritium instrument settings for the determination of phosphorus-32, iodine-131 and other isotopes. (See also Hoffman).⁵³

Problems. The Cerenkov light is highly directional and of heterogeneous wavelength. These problems have been approached by Haberer and Kölle^{45,46} who suggested the use of the water-soluble sodium salt of 1-naphthylamine 4-sulphonic acid as a wavelength 'shifter'. Its function is to absorb some of the directional ultraviolet radiation and re-emit it isotropically in the visible region. Läuchli⁸¹ reported the similar use of 7-amino 1,3-naphthalene disulphonic acid. Also, Elrick and Parker²⁸ have studied in detail the use of the double sodium, potassium salt of 2-naphthylamine disulphonic acid. Other improvements in detection efficiency can be achieved by the use of plastic vials.^{28,45,65,81}

Problems arising due to variation in refractive index^{46,28} and density²⁸ have been considered and Clausen¹⁶ reported on the effects of the presence of organic solvents, inorganic salts, acids, and alkalis, on the estimation of phosphorus-32. Similar investigations were made by Haviland and Bieber⁴⁹ (organic solvents) and by Johnson⁷² (isopropanol, ethanol, chloroform, and formic acid).

The method has proved to be almost entirely free from chemical quenching, but colour quenching can arise, although De Volpi *et al.*²² reported the counting of a pink manganese-56 solution without difficulty. The correction of colour quenching in Cerenkov counting lends itself to treatment by standard means. Francois³⁸ used internal standardization to measure potassium-42 in urine, and colour quench correction¹²⁹ curves have been used by various investigators¹⁴⁰ for phosphorus-32 and by Moir⁹³ for potassium-42 from biological materials. External standardization can be used as by Brownell and Läuchli¹⁰ for chlorine-36 and rubidium-86 in plant materials. Elrick and Parker²⁸ recommended radium-226 as the external γ -source. They critically reviewed the quench correction methods available and offered an alternative spectrophotometric method for samples possessing similar optical absorption spectra. These authors have provided excellent reviews on the theory and use of Cerenkov counting.^{102,103}

The method has been used, with success, to deal with large volumes of solution (Francois³⁸ for potassium-42 and Yamada¹⁴³ for strontium-90/yttrium-90) but Rippon¹¹⁰ considers it a not very suitable method for fission products in effluents. Other uses include

Table 5. Comparative studies.

Authors	Reference No.	Isotopes considered	Techniques compared
Aubouin	1	Phosphorus-32, sulphur-35, potassium-42, calcium-45, iron-59, strontium-90/yttrium-90, thallium-204	G.M. Plastic scintillator. Labyrinth plastic scintillator
Burt and Gibson	11	Chlorine-36, strontium-90/yttrium-90, caesium-137	Plastic beads, plastic flow cell, anthracene filled cell
Carr and Nolan	12	Calcium-45, strontium-85	G.M. Gas flow counters, scintillator beads, scintiglas, gel, glass fibre filter paper
Carr and Parsons	13	Calcium-45	Plastic scintillators. General review of liquid scintillation counting methods for calcium-45

the determination, by Braunsberg and Guyver,⁸ of phosphorus-32 and sodium-24 in tissue slices, of phosphorus-32 in chromatographic media by Haviland and Bieber,⁴⁹ and in tissue extracts by Threlfall *et al.*¹³¹ (See also Garrahan and Glynn).³⁹ Hoch *et al.*⁵² offered a method for iodine analysis in biological samples by neutron activation analysis followed by scintillation counting of Cerenkov radiation.

In conclusion, it can be said that Cerenkov counting offers a useful and convenient adjunct to the method of liquid scintillation and one might expect its use to grow considerably for β^- -emitting isotopes whose E_{\max} is > 0.5 MeV, i.e. high enough to produce detectable Cerenkov radiation.

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DISCUSSION

F. E. L. ten Haaf: Have you any experience with water-soluble scintillators? I think there has been a recent publication on this subject, but I have not yet found out the details.

A. Dyer: No, we have not tried this. The publication you refer to is presumably that of Haberer and Kolle, *Atompraxis* 11, 664 (1965) who refer to an improvement in the Cerenkov counting efficiency of certain β -emitters brought about by the addition of a water-soluble fluorescent compound to the aqueous solution.

B. E. Gordon: The paper by Leffingwell (T. P. Leffingwell *et al.*, *Intern. J. Appl. Radiation Isotopes* 13, 75 (1962)) reported an increased counting efficiency when colourless Fe^{+++} *ortho*-phenanthroline was converted to red Fe^{++} *ortho*-phenanthroline. This is impossible to explain by increased pulse height. This increase arose because the counter was set for carbon-14 counting and the red colour simply lowered the pulse height so that the peak shifted into the carbon-14 channel. A far better answer would be to leave the iron in the colourless ferric form as the *ortho*-phenanthroline complex, and open the upper discriminator to include the higher energy portion of the spectrum.

The only other answer I can think of is that uncomplexed *ortho*-phenanthroline is a far better chemical quencher than complexed Fe^{++} *ortho*-phenanthroline is a colour quencher. This is a less likely explanation.

B. W. Fox: What blender was used when chemiluminescence was observed?

A. Dyer: The chemiluminescence with zinc-65 and barium-133 occurred in a Hayes and Gould cocktail i.e. ethyl alcohol was the blending solvent. The zinc and barium were present as chlorides.

B. W. Fox: Comment: We have been interested in trying to find a solid peroxide scavenger to keep with solvents. We find that granulated zinc kills peroxides in dioxane and alkoxy-alcohols within 24 h.