

LIQUID SCINTILLATION COUNTING OF INORGANIC RADIOCHEMICALS IN
HIGH-EFFICIENCY SCINTILLATORS

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Methods of incorporating inorganic radiochemicals into liquid and sol-gel scintillators that exhibit high scintillation yield are described. Liquid-scintillation measurements have been made at the National Bureau of Standards on 31 different radionuclides for a variety of application in radionuclide metrology. Sample preparation techniques are described for a number of radionuclides that differ markedly in their chemical behavior as well as in their nuclear-decay characteristics. Particular emphasis is given to radionuclides such as ^{55}Fe and ^{241}Pu which decay by emission of low-energy radiations.

1. INTRODUCTION

For many years workers have been incorporating inorganic radiochemicals into liquid scintillators (Horrocks, 1962). In a recent review on this subject Coursey and Moghissi (1980) reported that 76 radionuclides of 57 different elements have been assayed using liquid-scintillation counting techniques. In the present work, scintillator formulations are reported for 23 elements which have been examined at the National Bureau of Standards (NBS). These 23 elements are indicated on the periodic chart in Figure 1.

For radionuclides of 9 of the elements in Figure 1, direct activity measurements were made in which the disintegration rate of the radionuclide is determined directly for each vial (NCRP, 1978). For accurate direct measurements of beta-particle emitters, the beta-particle counting efficiency must be as high as possible, and, consequently, scintillators that exhibit

a very high scintillation yield must be used. The scintillation yield can be slightly lower for direct measurements of alpha-particle emitters because the alpha particles, of several MeV each, give rise to large light pulses. The alpha-particle counting efficiency thus approaches 100% even for quenched samples (McDowell et al., 1979).

METALS														NONMETALS					
IA																			
H	IIA	TRANSITION METALS											IIIA	IVA	VIA	VIA	VIIA	He	
Li	Be												B	C	N	O	F	Ne	
No	Mg	IIIB	IVB	VB	VI B	VII B	VIII		IB	II B		Al	Si	P	S	Cl	Ar		
K	Ca	Sc	Ti	V	Cr	Mn	Fe	Co	Ni	Cu	Zn	Ga	Ge	As	Se	Br	Kr		
Rb	Sr	Y	Zr	Nb	Mo	Tc	Ru	Rh	Pd	Ag	Cd	In	Sn	Sb	Te	I	Xe		
Cs	Ba		Hf	Ta	W	Re	Os	Ir	Pt	Au	Hg	Tl	Pb	Bi	Po	At	Rn		
Fr	Ro																		
LANTHANIDE SERIES		La	Ce	Pr	Nd	Pm	Sm	Eu	Gd	Tb	Dy	Ho	Er	Tm	Yb	Lu			
ACTINIDE SERIES		Ac	Th	Pa	U	Np	Pu	Am	Cm	Bk	Cf	Es	Fm	Md	No	Lw			



DIRECT
ACTIVITY
MEASUREMENT



COMPARATIVE
ACTIVITY
MEASUREMENT



PRELIMINARY LS
MEASUREMENT

Fig. 1 Periodic chart of the elements showing the 23 elements for which scintillator formulations are reported in this work.

For comparative assays of beta-particle emitters, such as ^3H , ^{14}C and ^{63}Ni , vials prepared from a standard solution of the radionuclide are compared to those prepared from an unknown solution. It is not essential that the scintillation yield be exceptionally high for such comparative measurements; it is more important that the chemical compositions of the two solutions be the same, so that the type and degree of quenching will be the same for both unknown and standards vials.

The formulations that are reported here for 31 radionuclides have been developed over a period of about 6 years,

and, understandably, improvements have resulted from experience gained during this period. There has been no systematic effort made, however, to repeat earlier measurements simply to obtain slightly higher counting efficiencies. The scintillators reported here, therefore, may not be optimum, but they were satisfactory for the intended purpose.

As we have accumulated more data on scintillators it has proven useful to group radionuclides of elements in a given region of the periodic chart. This approach can save considerable time in designing scintillator formulations for additional radionuclides. This is demonstrated in the RESULTS AND DISCUSSION section in which radionuclides are divided into four groups: (3.1) *Alkali and Alkaline Earth Elements*, (3.2) *Transition Metal and Lanthanide-Series Elements*, (3.3) *Actinides*, and (3.4) *Non-Metals and Heavy Metals*.

2. EXPERIMENTAL

2.1 Equipment

Three liquid-scintillation systems have been used: (i) a $4\pi\beta$ (LS)- γ coincidence system, which employs a hemispherical cell placed above a single phototube (Lucas *et al.*, 1977), (ii) a system consisting of two RCA 8850* phototubes optically coupled to the ends of a cylindrical quartz spectrophotometer cell (Hutchinson *et al.*, 1978), and (iii) a Packard Model 3320 Tri-Carb.

2.2 Materials

Commercial solgel (emulsion) scintillators used were Aquasol II and Biofluor (New England Nuclear), Beckman GP (Beckman Instr.), and PCS (Amersham Corp.). Solvents used were *p*-xylene (ICN spectral grade) and toluene (Packard "Puresolv") and the scintillators were *p*-*bis*-(*o*-methylstyryl)-benzene (*bis*-MSB from Eastman Kodak) and 2-(4'-*t*-butylphenyl)-5-(4"-biphenyl)-1,3,4-oxadiazole (butyl-PBD from ICN). The chelating agent was di-2-ethylhexyl phosphoric acid (HDEHP) obtained from K&K Laboratories and used without further purification. Radionuclide solutions of known radioactivity concentration were supplied by other workers in the NBS Radioactivity Group (Mann, 1979).

*The mention of commercial instruments and scintillators in this work is not an endorsement by the National Bureau of Standards.

2.3 Methods

In a typical experiment, carriers and chelating agent are added to a flask containing 100 mL of solgel scintillator. If necessary, up to 5% water by volume may be added to insure dissolution of the carrier salts. This "buffered scintillator" is then pipetted into the special cells, in the case of systems (i) and (ii), or for the commercial counter (iii), into glass vials, which meet the dimensional requirements of the International Electrotechnical Commission standard (IEC, 1977). The aqueous sample, typically about 30 mg, is transferred gravimetrically to the cell and mixed with the scintillator (BIPM, 1975). It should be noted that these 30-mg aqueous samples contain only a few μg of carrier. Thus, the final emulsion will be carrier free unless additional carrier is added.

Counting efficiencies are reported here only for the Packard Tri-Carb, for 10 mL of scintillator in the standard vial at 60°C . In the usual operating mode, the outputs for the two phototubes are summed, with a coincidence requirement. The amplifier is set at high gain, and the counting rate is observed above a single discriminator set just above the noise level.

3. RESULTS AND DISCUSSION

3.1 Alkali and Alkaline Earth Elements

The scintillators that have been used for these Group IA and IIA elements are shown in Table I. Results are not given for ^3H as the applications of commercial solgel scintillators for counting ^3H -water are well-known (Benson, 1976). The Group IIA cations, Ca^{+2} , Sr^{+2} , Ba^{+2} and Ra^{+2} , are expected to present the greatest difficulties because they are nearly insoluble in organic solvents. They also have a tendency to exchange with surface sites on the walls of glass containers. Unsatisfactory results were initially obtained for ^{89}Sr in Aquasol II and PCS, because of insufficient carrier in the emulsion. Based on our experience with strontium we would now suggest adding 150 ppm of cation carrier to the solgel for strontium, barium and radium radioisotopes in order to passivate the surface sites on the walls of glass vials. For the radium radionuclides, ^{226}Ra and ^{228}Ra , stable barium carrier may be used.

The Group IA elements seem to present fewer problems. Vials containing ^{134}Cs in carrier-free PCS have been found to be stable for several months. Nevertheless, unless quenching by the carrier is a serious problem, it is probably still

worthwhile to add the appropriate alkali-halide carrier to the solgel before adding the aqueous sample. This is the method we have used most recently for ^{22}Na .

It appears that any of the commercial solgel scintillators can be modified for use with these radionuclides. Several workers for example, have used Insta-Gel (Packard Instr.): ^{86}Rb (Ishikawa and Takiue, 1973), ^{90}Sr - ^{90}Y (Randolph, 1975), and ^{226}Ra (Parks and Tsuboi, 1978).

Table I. Solgel Scintillators for the Alkali and Alkaline-Earth Elements

Radionuclide	Sample Solution (a)	Scintillator (b)	Typical Counting Efficiency (c)
^{22}Na	89 ppm Na^+ 2 N HCl	Beckman GE, 94 ppm Na^+ 7% water	99% for β^+
^{45}Ca	257 ppm Ca^{+2} 1 N HCl	PCS, 100 ppm Ca^{+2} 5% water	96%
^{89}Sr	100 ppm Sr^{+2} 1 N HCl	Aquasol II, 150 ppm Sr^{+2} 5% water, 0.01 M HDEHP	98%
^{90}Sr - ^{90}Y	50 ppm Sr^{+2} , 50 ppm Y^{+3} 1 N HCl	Biofluor, 120 ppm Sr^{+2} 4% water	98% ^{90}Sr 99% ^{90}Y
^{139}Cs	82 ppm Cs^+ 0.1 N HCl	PCS, carrier free 0.3% water	92%
^{140}Ba - ^{140}La	14 ppm Ba^{+2} 14 ppm La^{+3} 1 N HNO_3	PCS, carrier free 0.4% water	—
^{226}Ra + daughters	4 ppm Ba^{+2} 4 N HNO_3	PCS, carrier free 0.3% water, 0.05 M HDEHP	—

(a) ppm is defined here as μgrams of cation per gram of solution or emulsion.

(b) Water content is expressed as volume fraction of water (in %) after the sample is mixed with the scintillator.

(c) Counting efficiencies were not measured for the ^{140}Ba - ^{140}La , but they should be close to 100% for each. The ^{226}Ra decays by low-energy beta emission and the counting efficiency is low. However, the counting efficiency is nearly 100% for the daughter product, ^{226}Ac , and for its progeny.

3.2 Transition Metals and Lanthanide-Series Elements

There are a total of 41 elements in these two regions of the periodic chart. The results of our investigations with radionuclides of 10 of these elements are shown in Table II. For most of these elements it appears to be advantageous to add a chelating agent such as HDEHP to the scintillator

(McDowell, 1971; Horrocks, 1973). No problems with instability of the scintillators were observed for any of the radionuclides in Table II.

Table II. Sol-gel Scintillators for Transition-Metal and Lanthanide-Series Elements^(a)

Radionuclide	Sample Solution	Scintillator	Typical Counting Efficiency ^(c)
⁵⁴ Mn	50 ppm Mn ⁺² 2.5 N HCl	PCS, carrier free 1.2% water	---
⁵⁵ Fe	11 ppm Fe ⁺³ 5 N HNO ₃	PCS: p-xylene (1:1), 1 ppm Fe ⁺³ 0.4% water, 0.05 M HDEHP	35%
⁶⁰ Co	13 ppm Co ⁺² 4 M HCl	Biofluor, 27 ppm Co ⁺² 2.5% water	94%
⁶³ Ni	83 ppm Ni ⁺² 0.1 N HCl	PCS, 50 ppm Ni ⁺² 3.6% water, 0.05 M HDEHP	69%
⁹⁹ Mo- ^{99m} Tc	carrier free Mo ⁺⁶ , Tc ⁺⁷ 4 N HNO ₃	PCS, carrier free 0.3% water	---
^{99m} Tc	carrier-free Tc ⁺⁷ 4 N HCl	PCS, carrier free 0.3% water	100% for conversion electrons
¹⁴⁰ La	carrier-free La ⁺³ 2.5 N HNO ₃	PCS, carrier free 0.4% water	---
¹⁴⁷ Pm	carrier-free Pm ⁺³ 1 N HCl	PCS, carrier free 1% water	91%
¹⁵⁵ Eu	75 ppm Eu ⁺³ 2 N HCl	PCS, carrier free 5% water, 0.05 M HDEHP	90%
^{166m} Ho	2800 ppm Ho ⁺³ 4 N HCl	PCS, 37 ppm Ho ⁺³ ^(b) 1.2% water	---

(a) See footnotes (a) and (b) in Table I.

(b) This is the final Ho⁺³ concentration after addition of the sample to the scintillator.

(c) Efficiencies were not observed in the Tri-Carb for ⁵⁴Mn, ⁹⁹Mo, ¹⁴⁰La or ^{166m}Ho. For the beta-particle-emitters ⁹⁹Mo and ¹⁴⁰La, the counting efficiency should approach 100%.

Most of our work with transition metal radionuclides has been with ⁵⁵Fe and ⁶³Ni. The former decays by electron capture, for which the highest energy x-ray is 6.5 keV (Gibson and Marshall, 1972). The ⁶³Ni is a low-energy beta-particle emitter (E_{β} maximum of 65.87 keV). To prepare very high-efficiency scintillators for these two radionuclides, one must avoid using excess carrier because the yellow Fe⁺³ complex

in dilute HCl or HNO₃ solutions, and the blue-green Ni⁺² complex in dilute HCl, serve as color quenching agents in the scintillator. The highest counting efficiency observed for ⁵⁵Fe for the 10-mL vial was 45%. In this experiment the sample consisted of 17 ppm Fe⁺³ in 0.5 N HCl and the final solgel scintillator contained only 3 μg Fe⁺³ per 10 mL of emulsion. At such low carrier levels it may be necessary to coat the walls with a silicone compound to avoid plateout (BIPM, 1975).

The results for the lanthanides shown in Table II demonstrate that the solgel scintillators can be used for carrier-free samples, such as the ¹⁴⁷Pm, as well as for solutions containing high concentrations of carrier, such as the ^{166m}Ho. (The latter sample was prepared by dissolving a holmium target.) When practical, however, the solgel should be buffered with cation carrier (50 to 100 ppm) and HDEHP (about 0.01 M) before the sample is added.

3.3 Actinides

Table III shows the radionuclides of the three actinides examined so far at NBS. Sample preparation for alpha-particle counting by liquid-scintillation techniques has been discussed by McDowell (1971) and by McDowell and others at this conference. These workers suggest using a chelating agent to extract plutonium into an organic solvent suitable for liquid-scintillation counting. We have found that when a aqueous acidic sample of plutonium is added to a commercial solgel scintillator, it is also necessary to have the chelating agent present. Without the HDEHP the observed alpha-particle count rate may decrease by 5% per day. It is suggested that in the absence of the chelating agent, the Pu⁺⁴ polymerizes in the weak acid environment of the solgel. Conditions for polymerization of Pu⁺⁴ are discussed by Constanzo and Biggers (1963).

No problems were observed for uranium or americium radionuclides, but HDEHP was needed for the ²⁴³Am-²³⁹Np equilibrium mixture. Other solgel scintillators have been used for the actinides. Horrocks (1974) has described the use of Readsolv VI (Beckman Instr.) for normal uranium and Miglio (1978) has used Aquasol II for americium, curium and californium radionuclides.

²⁴¹Pu is of special interest because it decays primarily by low-energy beta-particle emission (E_β maximum of 20.6 keV) to ²⁴¹Am, which decays by alpha-particle emission. Our measurements with solgels and some limited solvent extraction experiments suggest that, when a mixture of ²⁴¹Pu - ²⁴¹Am is added to solgel containing HDEHP, the plutonium is extracted into the organic phase while the americium remains in the aqueous micelle.

As shown in Table III, the highest efficiency obtained for ^{241}Pu was 50%, and this was for an unquenched toluene-based scintillator.

Table III. Liquid and Solgel Scintillators for the Actinides^(a)

Radionuclide	Acid Form for Carrier-Free Sample Solution	Scintillator	Typical Counting Efficiency
^{235}U	U_3O_8 dissolved in 1 N HNO_3	PCS, 0.05 M HDEHP	100%
^{238}Pu , ^{239}Pu , ^{240}Pu	PuO_2 dissolved in 5 M HNO_3	PCS, 0.05 M HDEHP	100%
^{241}Pu (A)	PuO_2 dissolved in 5 M HNO_3	PCS, 0.05 M HDEHP	33%
(B)	Pu^{+4} -HDEHP in toluene	toluene, 0.05 M HDEHP 9.2 g/l butyl-PBD 0.8 g/l bis-MBS	50%
^{241}Am , ^{243}Am - ^{239}Np	Am^{+3} in 5 M HNO_3	PCS, 0.05 M HDEHP	100% for α particles ^(b)

(a) See footnotes (a) and (b) in Table I.

(b) Counting efficiency for ^{239}Np beta particles is also close to 100%.

3.4 Non-Metals and Heavy Metals

Very little liquid-scintillation work has been done at NBS on radionuclides of elements in this region of the periodic chart, and the three examples shown in Table IV (carbon, chlorine and tin) are certainly not representative. References are given, however, in the review article referred to previously (Coursey and Moghissi, 1980) for 28 radionuclides of elements in this region.

The development of the high-efficiency scintillator shown in Table IV for $^{121\text{m}}\text{Sn}$ is described in Hutchinson *et al.* (1978). It was necessary to use toluene instead of *p*-xylene as the solvent for these samples, because the phototubes were cooled below the melting point of *p*-xylene (13.5°C).

The ^{14}C sample composition shown in Table IV is that of the NBS Standard Reference Material 4246. If this material is deposited directly into a commercial solgel scintillator (PCS, Beckman GP and Biofluor were all used.) up to 30% of the ^{14}C may escape into the gas phase above the scintillator. According to Kobayashi (1979) this occurs because the

general purpose solgels are in an acidic form, so that they can accomodate alkaline biological samples, without exhibiting excessive chemiluminescence. As shown in Table IV, the solgel can be made suitable for counting Na_2CO_3 , if it is first neutralized with NaOH and ethanolamine. After addition of alkali, however, one should check for chemiluminescence.

Table IV. Liquid and Solgel Scintillators used for ^{14}C , ^{36}Cl , and $^{121\text{m}}\text{Sn}$ (a)

Radionuclide	Sample Solution	Scintillator	Typical Counting Efficiency
^{14}C	2120 ppm Na_2CO_3 0.001 N NaOH	Beckman GP 190 ppm ethanolamine 200 ppm NaOH 90 ppm Na_2CO_3 5% water	93%
^{36}Cl	120 ppm Cl^- 0.093 M NaCl	PCS, carrier free 0.4% water	99%
$^{121\text{m}}\text{Sn}$	Sn^{+4} - HDEHP in toluene	Toluene, 0.004 M HDEHP 8 g/l butyl-PBD 0.5 g/l bis-MSB 200 ppm Sn^{+4}	(b)

(a) See footnotes (a) and (b) in Table I.

(b) The decay scheme and observed spectra for $^{121\text{m}}\text{Sn}$ are described in Hutchinson *et al.* (1978).

4. SUMMARY

Formulations have been described which have proven useful in dissolving inorganic radiochemicals of 23 different elements in liquid and solgel scintillators. These should not be considered as recipes, however, as slight changes in chemical and physical conditions may have marked effects on the stability of the formulation. For example, three variables that must be considered are: the quality control for commercial emulsions, the temperature at which samples are counted, and the different ion-exchange properties of surfaces for different types (or batches) of vials. With these cautions in mind, however, it still appears that commercial solgel scintillators can be adapted for use with a large number of radionuclides, providing optimum levels of carrier and chelating agents are established.

For measurements such as those described here, which involve very small aqueous samples, the general-purpose solgel scintillators do have a drawback in that they contain excess emulsifiers. The manufacturers should be able to develop products that exhibit >50% counting efficiency for 20 mg of

^3H -water. The results presented in other papers at this conference suggest that such materials may soon be available.

5. ACKNOWLEDGMENT

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DISCUSSION

B.E. Gordon. Have you tried using a gel scintillator for ^{55}Fe ? This would allow you to incorporate more Fe^{+3} into the system.

B.M. Coursey. No. We have not used gel scintillators because the scintillation yields are too low for these systems. It is certainly true that gel systems can incorporate more iron, and this is an advantage for low-level and biological assays of ^{55}Fe . However, to obtain the maximum counting efficiency, concentrations of all quenching agents, including water, surfactant, and Fe^{+3} , must be as low as possible.

W.J. McDowell. I would like to make the comment that another useful class of chelating agents for the trivalent actinides are the high-molecular-weight quaternary ammonium chlorides. Two examples of these materials which are commercially available are Adogen 464 and Aliquat 336.