

Measurement of ^{90}Sr in Reactor Wastes by Cerenkov Counting of ^{90}Y

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Determination of ^{90}Sr in low-level radioactive wastes (LLW) from reactors is difficult because of the presence of so many other radionuclides in samples of interest. This problem was dealt with by radiochemical separation of strontium followed by yttrium separation and Cerenkov counting of the high-energy β -particle emissions of ^{90}Y in order to quantitate ^{90}Sr . Separation of this important nuclide in low-level waste samples was by solvent extraction using tri-n-butyl phosphate. Since most beta emitters in LLW from commercial nuclear power facilities are below about 1 MeV, Cerenkov counting with a high-discriminator setting provided accurate quantitation without interference of potential contaminants which were either removed by separation or discriminated against by the counting procedure. A tracer of ^{85}Sr was used and the radiochemical yield was $59.6 \pm 1.9\%$; the lower limit of detection was found to be 1.48 pCi/g based on a 10 g sample and a 20-min counting time.

Introduction

Determination of the potential environmental impact of a site used for disposal of low-level radioactive wastes should consider several important long-lived nuclides. Strontium-90 is one of the important constituents of low-level radioactive waste (LLW) from nuclear power plants, and for this reason merits attention in establishing the source term for shallow land burial sites. Several groups of states have formed regional compacts to dispose of LLW in accordance with the Low-Level Waste Policy Act of 1980 (USC80) and Federal regulations (NRC82); therefore, accurate site inventories of ^{90}Sr and other long-lived radionuclides in LLW are necessary for siting and operating such disposal facilities.

Strontium-90 has a half life of 28.1 y (Kocher, 1981) and is a pure β -particle emitter with a maximum beta energy of 546 keV. Its primary mechanism of production is by thermal neutron fission of ^{235}U and ^{239}Pu in nuclear reactors. The thermal fission yield of ^{90}Sr for ^{235}U is 5.9%; thus, nuclear power plants represent a significant source of ^{90}Sr production. ^{90}Sr can also occur by successive neutron activation of stable ^{87}Sr and ^{88}Sr ; however, these hardly exist in fuel or as trace constituents in reactor structures, and the activation cross sections are very small. The cross section of the fission product ^{89}Sr is also low (0.42 barn); consequently, production of ^{90}Sr by neutron activation can be considered insignificant compared to fission. Strontium-90 decays to ^{90}Y which decays 99.98% of the time by emission of β particles with maximum energy of 2283 keV. The half

life of ^{90}Y is 64 h and for most practical purposes it is always in equilibrium with ^{90}Sr , a significant and useful feature for measurement of sources of ^{90}Sr .

Various analytical procedures have been used to measure ^{90}Sr in samples. Lieberman (1984) and Volchok and dePlanque (1982) present methods for measuring ^{89}Sr and ^{90}Sr in environmental samples. Most methods depend on radiochemical separation of Sr followed by proportional counting to measure ^{89}Sr , followed by assay of ^{90}Y ingrowth to measure ^{90}Sr . The γ -ray emitter ^{85}Sr is often used as a tracer for measuring chemical recovery. Several authors (Piltingsrud and Stencel, 1972; Parker and Elrick, 1970; Randolph, 1975; Ross, 1971) report the use of liquid-scintillation counting for measuring ^{89}Sr , and ^{90}Sr , including various techniques for unfolding mixed beta spectra of ^{89}Sr and ^{90}Sr , and ^{90}Y .

Although reliable procedures exist for measuring ^{90}Sr in environmental samples, a procedure for dealing with sample contamination by the diversity of radionuclides in LLW samples from reactors has not been reported. It has been observed (Martin, 1985, 1986) that reactor waste streams contain numerous beta emitters that could interfere with the accuracy of ^{90}Sr measurements. It is important, therefore, to assure that measured concentrations represent ^{90}Sr and not a contaminant artifact; thus, either very pure separations are required or a method to subtract contaminants is needed. Since ^{89}Sr , with a half life of 50.5 d, is also commonly present in reactor LLW it is also necessary to assure that measurements of ^{90}Sr account for this isotope in order not to overreport

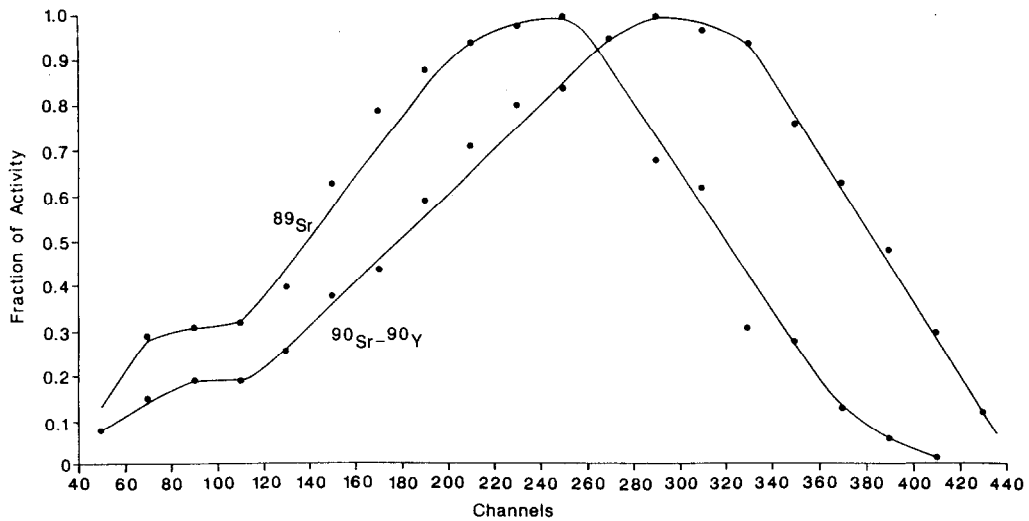


Fig. 1. Liquid scintillation analyzer (Beckman Model LS 6800) Cerenkov spectra of ^{89}Sr and ^{90}Sr - ^{90}Y standard.

^{90}Sr concentrations. The fission yields of ^{89}Sr and ^{90}Sr are 4.8 and 5.9%, respectively and both are present in LLW streams. The ratio of the isotopes varies due to differing ages of wastes when shipped; however, ^{89}Sr is of little significance as a LLW source term for disposal sites since it soon decays away after disposal.

Since the primary source of ^{90}Sr in LLW is nuclear reactor waste streams, it is important that the method be applicable to quantitating the concentrations of ^{90}Sr in the various liquid and solid media such wastes comprise. The objectives of this study were to develop a reliable procedure for determining ^{90}Sr in LLW from reactors in the presence of ^{89}Sr and beta-emitting contaminants and to establish its general applicability for measuring ^{90}Sr in LLW from reactors. Although these studies did not consider ^{90}Sr in other non-fuel-cycle LLW, such as that from research and medical institutions, the same methodology and approach are believed to be applicable for these wastes.

Theory

For disposal of LLW containing strontium, we are concerned only with ^{90}Sr content; because its short-lived equilibrium product ^{90}Y emits high energy β particles we may take advantage of this phenomenon by Cerenkov counting to discriminate against other beta emitters that may contaminate separated samples. Cerenkov counting for Sr measurements can be done by separating Y and counting it. This offers promise for analyzing LLW samples because even though such samples contain many complex beta emitters, most of these have maximum beta energies below about 1 MeV (Hudson, 1983; Farrell and Hudson, 1985). Yttrium-90 is the only radioactive isotope of Y that would be present from such a separation, and its beta energy of 2283 keV is ideal

for Cerenkov counting (Francois, 1973). Since Y is separated from Sr, it is necessary that the procedure also account for any trace carryover of Sr, especially ^{89}Sr . Whereas ^{90}Sr β particles barely produce Cerenkov radiation, ^{89}Sr which emits β particles up to 1488 keV, produces Cerenkov radiation that is of the same order as that from ^{90}Y as shown by the Cerenkov spectra of these nuclides in Fig. 1. It is impractical to discriminate against all ^{89}Sr betas by Cerenkov counting of ^{90}Y , even with high-energy window settings on the liquid-scintillation analyzer; however, it is possible to set a high-energy window for counting mostly ^{90}Y β particles which would discriminate against any ^{90}Sr betas, a large fraction of ^{89}Sr β particles, and apparently all other LLW beta emitters of concern. The combination of Sr separation, followed by Y separation and Cerenkov counting of ^{90}Y with a high-energy-window setting provides, therefore, an approach whereby ^{90}Y can be used to quantitate ^{90}Sr .

Method

The analytical method for ^{90}Sr analyses was designed for processing samples of LLW types representing about 6 months operation at the Big Rock Point and Palisades Nuclear Plants in Michigan. Detailed summaries of the types of samples analyzed have been reported for these plants and others by Martin (1985), but for the most part they comprise clean and dirty liquids, resins, filters, and smears. The samples are received as collected with no sample pretreatment for Sr provided during collection.

Radiochemical procedure

The procedure in HASL 300 (Volchok and de

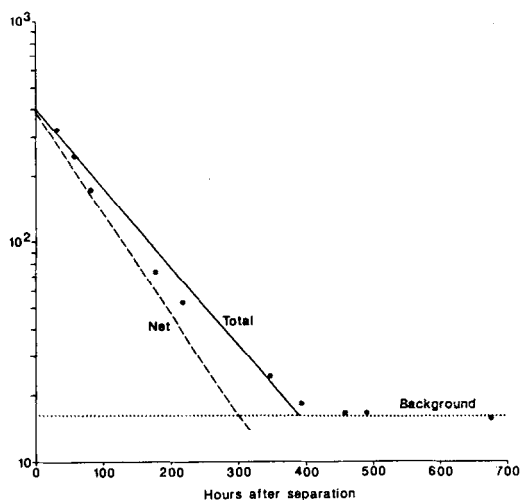


Fig. 2. Cerenkov count-rate decay curve of ^{90}Y separation from ^{90}Sr - ^{90}Y standard using high-energy discrimination

Planque, 1982) was modified for separation of ^{90}Sr from mixed activation, corrosion, and fission products. Solid samples such as resin beads, crude samples, liquids containing solids, and filters were added to a beaker containing 1 mL of 20 mg/mL Sr carrier, 1 mL of 10 mg/mL Y carrier (in nitrate solutions) and a ^{85}Sr tracer to determine chemical recovery. The samples were treated with 9M hydrochloric and concentrated perchloric acids, the solution was evaporated, and the residue was dissolved in 10 mL of distilled water. Liquid samples without solid fractions were added to a beaker with Sr and Y carriers and the ^{85}Sr tracer and evaporated to approximately 10 mL. It was not necessary to standardize the ^{85}Sr tracer since identical volumes added to each sample were counted by a single channel analyzer with a 2×2 -in. NaI(Tl) crystal before and after separation, and the ratio of these counts was the chemical recovery. Care was taken to minimize dead-time losses and to maintain identical counting geometries.

After pretreatment, 50 mL of concentrated nitric acid was added to each sample to destroy any remaining particulate material and evaporated again to 10 mL. Then 40 mL of concentrated nitric acid was added and the sample was cooled to room temperature. Tri-n-butyl phosphate (TBP) was equilibrated for separation by adding an equal volume of 14M nitric acid and shaking for 1 min. The aqueous layer was removed and discarded. The sample was transferred to a separatory funnel containing 50 mL of the equilibrated TBP, and was shaken for 5 min. The phases were allowed to separate, and the aqueous layer was transferred to a clean separatory funnel containing another 50 mL of equilibrated TBP. The time of transfer was recorded as the time of separation of Sr from Y. The separatory funnel was shaken for another 5 min and the phases were allowed to separate. The aqueous phase was discarded

and the TBP fractions were combined in a separatory funnel. The organic phases were shaken twice for 3 min each with 50 mL of 14M nitric acid to remove contaminants. The ^{90}Y was stripped from the TBP with two 50 mL portions of water and the aqueous portions were evaporated to less than 20 mL and transferred to a scintillation vial using 5M nitric acid. Care was taken to avoid evaporating the sample to near dryness since it was difficult to dissolve the solid material that formed. Figure 1 shows a plot of the Cerenkov spectra of a ^{90}Sr - ^{90}Y standard and a ^{89}Sr standard (without quench correction) determined with a Beckman LS 6800 Liquid Scintillation Analyzer (Beckman Inc., Irvine, Calif.) which has a logarithmic amplifier.

The ^{90}Sr activity per gram of sample, $A(^{90}\text{Sr})$, was calculated by:

$$A(^{90}\text{Sr}) = \frac{C_{\text{net}}}{E W Y 2.22 \times 10^{12} \text{ d/m-Ci}}$$

where C_{net} is the net beta count rate (cpm) of the ^{90}Y separation with background subtracted (based on a counting time of 20 min), E is the ^{90}Y counting efficiency, W is the sample weight, and Y is the chemical yield based on the decay-corrected count rate of the ^{85}Sr in the processed sample divided by the count rate of the ^{85}Sr spike (100% recovery). It was not necessary to store the samples for decay since ^{85}Sr decays by electron capture yielding a 514-keV γ -ray, neither of which interfered with the Cerenkov counting of the ^{90}Y β particles at the discriminator settings used.

Results and Discussion

By performing Cerenkov counting of ^{90}Y β particles with a high energy-window setting on the LSA it was possible to identify ^{90}Y , to quantitate it, and to selectively subtract any high-energy-beta-emitting contaminants that may have been present in the separated samples. These features were accomplished by constructing a traditional beta decay curve as

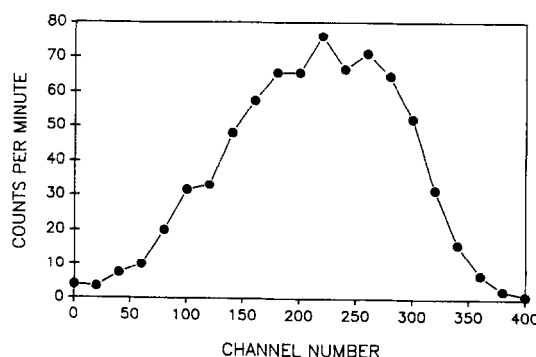


Fig. 3. Liquid scintillation analyzer (Beckman Model LS 6800) Cerenkov spectrum of ^{60}Co standard in H_2O indicating counts above discriminator setting of 240 channels.

shown in Fig. 2. The slope of the decay curve was used to verify that the half life was that of ^{90}Y ; extrapolating the curve back to time of separation ($t = 0$) and subtracting the residual background (also extrapolated to $t = 0$) yielded the net count rate of ^{90}Y at time of separation. If the residual background was high, its slope could be used to indicate the identify of the contaminant, if desired. It can take several weeks to do the latter; however, essentially all the separated ^{90}Y will have decayed in about 3–4 weeks, a period of time that is compatible with the time required to analyze all the other components of LLW samples. Initial success with these separations has been good, and the procedure of fully decaying the sample may prove to be an extra caution that can be considerably reduced.

The experimental procedure used was orders of magnitude more sensitive than the level of 0.004 Ci/m^3 required by 10 CFR 61 for LLW waste characterization (U.S. Nuclear Regulatory Commission, 1982). The chemical yield of the procedure was $59.6 \pm 1.9\%$ and the Cerenkov counting efficiency was determined by a standard (U.S. Environmental Protection Agency, Las Vegas, Nev.) to be 34% in water at the energy-window settings used, which were fairly high in order to discriminate against other potential beta-emitting contaminants. Other authors (Randolph, 1975; Parker and Elrick, 1970) report higher counting efficiencies in the range of 50%; the difference appears to be due to difference in window settings. Background counts with processed blanks were about 14–16 cpm, which with a 20-min counting time yielded a minimum detectable activity (Currie, 1968) of about 1.48 pCi/g for a 10 g sample at 59.6% recovery. Longer counting times would, of course, improve this minimum level.

Sample contaminants

Because LLW samples contain significant radioactivity from numerous nuclides, the presence of contaminants is always possible, even after chemical separation. Colbalt-60 is the most common nuclide found after radiochemical separations, probably because it represents the highest measured concentration in most LLW samples and because of its chemical properties. A minimal number of counts due to ^{60}Co occurs in Cerenkov counting at the settings used as shown in Fig. 3 presumably due to Compton electrons; however, this amounts to a total counting efficiency of less than about 2%. Discrimination of ^{90}Sr from trace amounts of ^{60}Co and other contaminants was confirmed by observing the decay of samples for about four weeks to establish the residual background. Liquid-scintillation counting of the samples in PCS (Amersham, Arlington Heights, Ill.) was also used to determine that some samples contained other beta-emitting contaminants, but the energies of these were low enough not to interfere significantly in the Cerenkov counting windows used.

Cerenkov counting also allowed discrimination against the most likely contaminant, ^{60}Co ; therefore, it did not interfere with the analyses using this method.

Summary and Conclusions

This study was undertaken to develop a methodology for measuring ^{90}Sr in various liquid, solid, and semi-solid low level radioactive waste samples. A radiochemical separation of Sr and Y by solvent extraction in tri-n-butyl phosphate followed by Cerenkov counting of ^{90}Y β particles in H_2O provided excellent determination of ^{90}Sr in the presence of mixed activation, corrosion, and fission products for the usual forms of reactor LLW that require classification. Good recoveries of ^{90}Y were obtained with yields of about $59.6 \pm 1.9\%$ and the combined method eliminated any significant interference by the myriad of other constituents in the LLW samples. Strontium-85, as an electron-capture, gamma-emitting nuclide, was found to be a useful tracer for determining chemical recovery because its decay does not interfere with the Cerenkov counting of ^{90}Y , even if it carries over with the Y separation. Cerenkov counting of processed samples allowed reliable detection of ^{90}Sr concentrations (from ^{90}Y) in LLW samples of 1.48 pCi/g based on a 10 g sample and 59.6% chemical recovery.

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