Measurement of ^{55}Fe in Reactor Samples by an Intrinsic Germanium Detector

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Determination of ^{55}Fe in reactor samples requires some care because of the low-energy x-rays emitted following decay by electron capture and the presence of ^{59}Fe and other possible γ-ray emitting contaminants in radiochemical separations. This problem was dealt with by radiochemical separation of Fe followed by use of an intrinsic germanium detector operated at high amplifier gain to count the low-energy x-ray emissions to quantitate ^{55}Fe. Separation of this important nuclide in reactor samples was by solvent extraction using triisooctylamine in xylene. Low-energy photon counting was done with a high gain setting and a 3 μs shaping time, which provided accurate quantitation without interference of ^{59}Fe and other potential contaminants, which were either removed by separation or discriminated against by the counting procedure. Iron-59, either present in the sample or added as a spike, was used as a tracer for determining radiochemical yield, which was about 70%. The lower limit of detection was found to be 80 pCi/g based on a 10 g sample and a 5 min counting time.

Introduction

Iron-55 is a common constituent of radioactive samples in nuclear power plants, and for this reason merits quantitation to determine potential contamination of work areas and as a source term for releases to the environment. Iron-55 has a half life of 2.72 ± 0.02 y (NCRP, 1985), and decays solely by electron capture followed by emission by the ^{55}Mn daughter of characteristic x rays of 5.89, 5.90 and 6.49 keV. Production of ^{55}Fe occurs by neutron activation of stable ^{54}Fe which exists in many reactor components at a natural abundance of 5.8%. The activation cross section of ^{54}Fe is 2.3 barn, consequently production of ^{55}Fe in nuclear power plants can be considered a significant potential source of exposure to workers (Farrell and Hudson, 1985) and the public (Palmer and Beasley, 1967). Because the half life is only 2.72 y, ^{55}Fe is for most practical purposes of minor significance in disposal of low-level radioactive wastes (LLW) because it decays away in two decades or so.

Various analytical procedures have been used to measure ^{55}Fe in a variety of samples. Lieberman (1984) and Volchok and de Planque (1982) present methods for its measurement in environmental samples. Most methods depend on radiochemical separation of Fe followed by photon counting with a thin NaI(Tl) crystal. The γ-ray emitter, ^{59}Fe, is often used as a tracer for measuring chemical recovery. Several authors (Gibson and Marshall, 1972; Grau, 1982; Horrocks, 1971; Steyn, 1967) report the use of liquid-scintillation counting (LSC) for measuring ^{55}Fe. Hor-rocks (1971) states that LSC analysis should yield up to 90% counting efficiency due to the mode of production of x rays and Auger electrons accompanying electron capture decay; however, Gibson and Marshall (1972) take exception to this report and indicate that an efficiency closer to 30% is more reasonable. Lowenthal *et al.* (1982) report the use of a 4 π proportional counter to count the low energy x rays from the decay of ^{55}Fe. Use of either of these two counting procedures for ^{55}Fe after chemical separation would be useful where contaminants are minimal.

Although reliable counting procedures exist for measuring ^{55}Fe in environmental samples, a procedure is also needed for dealing with the presence of ^{59}Fe and other potential sample contamination by the diversity of radionuclides in samples from reactors. It has been observed (Martin, 1985, 1986) that reactor waste streams contain numerous radionuclides that could produce low-energy emissions that interfere with the accuracy of ^{55}Fe measurements especially if a method based on LSC is used. Since ^{59}Fe, with a half life of 44.51 days (NCRP, 1985), is also commonly present in reactor samples, it is also necessary to assure that measurements of ^{55}Fe account for this radioisotope. The objectives of this study were to develop a reliable procedure for determining ^{55}Fe in a wide array of liquid and solid samples from reactors in the presence of ^{59}Fe and other low-energy photon-emitting contaminants and to establish its general applicability with conventional γ-ray spectroscopy equipment.

Method

The analytical method for ^{55}Fe analyses was designed for processing typical samples from 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 Fe provided during collection.

Radiochemical procedure

The concentration of ^{59}Fe was first quantitated, if present, in the sample before any analysis. If present, it was either used for tracer purposes or supplemented with additional ^{59}Fe standard. The procedure for separation of ^{55}Fe was adapted from HASL 300 (Volchok and de Planque, 1982). Solid samples such as resin beads, crud samples, liquids containing solids and filters were added to a beaker containing 1 mL of 5 mg/mL Fe carrier (in nitrate solution) and a ^{59}Fe tracer (if indicated) to determine chemical recovery. Liquid samples with solids and solid samples were treated with 9M hydrochloric and concentrated perchloric acids, and the resulting solution was evaporated to less than 5 mL. Liquid samples without solid fractions were added to a beaker with Fe carrier and the ^{59}Fe tracer and evaporated to approximately 5 mL. It was not necessary to standardize the ^{59}Fe 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. The ^{59}Fe emits several gamma photons, the two principal ones being of relatively high energy at 1099.3 and 1291.6 keV; these present minimal interference with counting of the low energy x rays from ^{55}Fe with the method used. Care was also taken to minimize dead-time losses and to maintain identical counting geometries.

After pretreatment and the addition of the Fe carrier and tracer, 50 mL of 6 M hydrochloric acid was added to each sample in a separatory funnel. Then 20 mL of 20% triisooctylamine in xylene (a 20:80 volume ratio) was added, and the sample was shaken for 5 min and the aqueous layer was discarded. The sample was then washed twice with 10 mL of 6 M hydrochloric acid, shaken for 1 min each, and the aqueous layer was removed and discarded. The sample was transferred to a beaker containing 10 mL of concentrated ammonium hydroxide and was stirred for 1 h. The stirred solution was filtered using a 2μm AE type membrane filter (Gelman Sciences, Inc., Ann Arbor, Mich.), and the filter allowed to dry for counting.

Counting procedure

A high purity intrinsic germanium detector was used for counting the ^{59}Fe tracer, for identifying any interfering γ-ray emitters, and for identifying and quantitating ^{55}Fe in processed samples. The ^{55}Fe procedure required an increase in amplifier gain and removal of the protective cap over the germanium window of the detector; the other assays were performed with conventional amplifier settings using 4096 data channels.

For ^{55}Fe counting, the course amplifier gain was increased from 20 to 1000 and the fine grain from 0.790 to 1.00. Since the energies of the ^{55}Mn characteristic x rays following ^{55}Fe decay are only 5.89 6.49 keV, it was also necessary to remove the protective cap from the detector. This was done very carefully because the detector can be very easily damaged in this mode. To prevent contamination, a sheet of paper was lowered onto the bare, vertically-oriented detector with a piece of string. The filters containing the separated Fe were allowed to dry and a piece of string was taped to the back of each. The filter samples were placed on or removed from the detector (covered with paper) by lowering or raising them with the string to avoid any possible touching of the detector by the fingers or the hands. A lead cap was placed over the chamber to maintain a low background during counting. The multichannel analyzer was set for 2048 channels. Figure 1 shows three x-ray spectra of a standard of ^{55}Fe determined for different shaping times with a Nuclear Data 6700 Multichannel Analyzer and associated software (Nuclear Data Inc., Schaumberg, Ill.) with higher amplifier gain. The ^{55}Fe activity per sample was calculated from the net photon count rate (counts s^{-1}) of the sample with background subtracted (based on a counting time of 5 min) after adjustment for the ^{55}Fe peak counting efficiency and the chemical yield.

Results and Discussion

It was possible to use an intrinsic germanium detector with high amplifier gain to identify and quantitate ^{55}Fe by counting the ^{55}Mn characteristic x rays which follow its electron capture decay and to selectively subtract any high energy γ-ray emitting
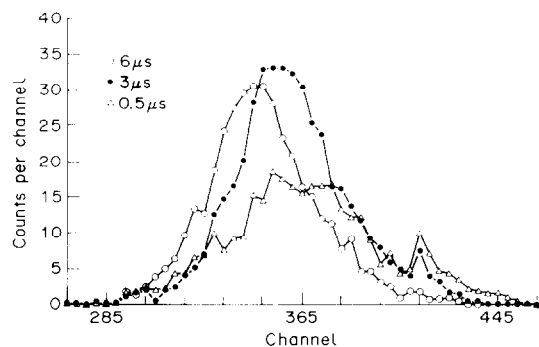

Fig. 1. x-Ray spectra of a flat ^{55}Fe standard at shaping times of 6, 3, and 0.5 μs.

contaminants that may have been present in the separated samples. The shaping time of the pulses was optimized by constructing several x-ray spectra of a ^{55}Fe standard at different settings, three of which are shown in Fig. 1. A shaping time of 3 μs gave the best resolution and highest efficiency. If the residual background at the peak is high, counting the sample at normal settings can be used to indicate the identity of the gamma emitting contaminant(s) that produce the counts in the peak region, usually due to Compton scattered photons. Initial success with these separations has been good, and the procedure of quantitating ^{55}Fe in the presence of other photon emitters has been successful with good sensitivity for a wide range of reactor samples, including radioactive waste samples. The chemical yield of the procedure was about 70% and the peak area photon counting efficiency was determined by a standard (U.S. Environmental Protection Agency, Las Vegas, Nev.) to be 1.04%. Background counts over the ^{55}Fe peak region with processed blanks were about 200 counts in 5 min which yielded a minimum detectable activity (Currie, 1968) of about 80 pCi/g for a 10 g sample at 70% recovery. Longer counting times would, of course, improve this minimum level.

Sample contaminants

Because reactor samples typically contain significant radioactivity from numerous nuclides, the presence of contaminants is always possible, even after chemical separation. Cobalt-60 is the most common nuclide found after radiochemical separations, probably because it represents the highest measured concentration in most reactor samples and because of its chemical properties. A minimal number of ^{60}Co counts due to Compton interactions are registered in the ^{55}Fe peak at the settings used. More important, the counts due to either ^{59}Fe or ^{60}Co were uniform over the ^{55}Fe peak region which would only increase the background, thus affecting the minimum detectable activity of the analysis. Good discrimination of ^{55}Fe from trace amounts of ^{60}Co and other contaminants was confirmed by observing the spectra of separated samples.

Summary and Conclusions

This study was undertaken to develop a methodology for measuring ^{55}Fe in various liquid, solid, and semi-solid reactor samples using a high purity intrinsic germanium detector. A radiochemical separation of Fe by solvent extraction into triisooctylamine in xylene followed by counting of low energy characteristic x rays provided good determination of ^{55}Fe in the presence of mixed activation,

corrosion, and fission products in typical reactor samples. Good recoveries of ^{55}Fe were obtained with yields of about 70%, and the combined method eliminated any significant interference by the myriad of other constituents in the samples. Iron-59 was found to be a useful tracer for determining chemical recovery because its γ-ray emissions did not interfere significantly with the photon counting of ^{55}Fe. Low-energy photon counting of processed samples by an intrinsic germanium detector with high grain allowed reliable detection of ^{55}Fe concentrations at a lower level of detection of 80 pCi/g based on a 10 g sample, 70% chemical recovery, and a 5 min counting time.

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