Interlaboratory Study to Validate a Procedure for the Determination of Strontium-89/Strontium-90 in Water

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Introduction

Radioactive contamination is significant on and around numerous U.S. Department of Energy (DOE) sites. More than 3,000 inactive waste sites have been identified on DOE property [1,2], many of which are contaminated with radionuclides. Radiostrontium (^{90}Sr and ^{89}Sr) has been identified as a significant source of contamination at several of these DOE sites [3]. To support cleanup efforts at these sites, innovative analytical methods are under development.

In the traditional strontium separation method [4], the Group IIa elements are first separated from the matrix constituents through a carbonate precipitation. Calcium is removed through repetitive precipitations of strontium nitrate using fuming nitric acid, whereas barium and radium are separated as the chromates. The ^{90}Y daughter of ^{90}Sr then is eliminated through a hydroxide precipitation. The purified strontium fraction is allowed to age; and, finally, ^{90}Y is isolated as an oxalate for beta counting. Clearly, this traditional procedure is hazardous, costly, and lengthy. Moreover, this method generates large quantities of secondary wastes, and there are many sources of error.

Recently, a method based on extraction chromatography [5,6] has been described for the determination of radiostrontium in environmental samples. This approach provides the specificity of solvent extraction with the convenience of column chromatography. Additionally, this method has the potential to be much faster and to generate significantly less secondary wastes than does the traditional method; however, for this approach to be widely accepted, it must first be validated. Therefore, this interlaboratory study was undertaken.

Experimental

Method Description

The procedure that was validated in this study, "Purification of Strontium in Water before Strontium-89/Strontium-90 Measurement," Method RP500 in the *Compendium of DOE Methods for Evaluating Environmental and Waste Management Samples* (DOE/EM-0089T, rev. 2), consists of preconcentration of the aqueous sample by one of four

methods (evaporation, cation exchange, calcium phosphate precipitation, or calcium carbonate precipitation), purification of the preconcentrated material by using an ElChrom Sr resin column, and measurement of the ^{89}Sr and ^{90}Sr by one of three counting procedures (liquid scintillation counting, gas proportional counting, or Cerenkov counting). For this study three of the four preconcentration methods, cation exchange, calcium phosphate precipitation, and calcium carbonate precipitation, were evaluated by each participating laboratory. The levels of ^{89}Sr and ^{90}Sr were measured either by gas proportional counting or by Cerenkov counting. Liquid scintillation counting was not chosen by any of the participating laboratories.

Selection of Participants

Participants were selected on the basis of proposals submitted in response to a competitive request for proposal (RFP) that was sent to 40 laboratories. Availability of the RFP was also announced publicly to include all potential bidders. Thirteen proposals were received in response to the RFP. Criteria for selection included prior experience assaying ^{89}Sr and ^{90}Sr, qualifications of personnel, results of performance evaluations, the adequacy of internal standard operating procedures (SOPs) for use of equipment and applicable procedures, and costs. The six lowest-priced technically qualified proposals were selected to participate in the study.

Preparation of Materials for the Interlaboratory Study

Rust Geotech, Inc., obtained standard solutions of ^{89}Sr and ^{90}Sr from Analytics, Inc., with radioactivity levels certified by the vendor to be traceable to National Institute of Standards and Technology (NIST) standards. The 5-mL standards were diluted to 1 L with 0.08 M nitric acid to prepare working standards of ^{89}Sr at 105 pCi/mL and ^{90}Sr at 194 pCi/mL. The working standards were used to prepare 15 L each of seven water samples with different activities of the ^{89}Sr and ^{90}Sr. The experiment was designed so that there was no correlation between the ^{89}Sr and ^{90}Sr activities. The samples were preserved by acidification with 5mL of 70% nitric acid per liter of sample. The prepared samples were dispensed into plastic bottles labeled with the sample identification, bottle number, nitric acid concentration, and the reference date indicated as the preparation date.

One 1,500-mL bottle of each sample was shipped to five of the laboratories, and two 750-mL bottles of each sample were shipped to the sixth laboratory to conform to the International Air Transport Association's specifications for corrosive liquids. One set of bottles was reserved for analysis by Rust Geotech Laboratory.

The uncertainties on the certified values of the ^{89}Sr and ^{90}Sr stock standard provided by the vendor were 3.5% and 5.0%, respectively. No more than 1% additional uncertainty is estimated to result from the dilution of the stock standard and preparation of the samples. Therefore, the total uncertainties on the calculated concentration of ^{89}Sr and ^{90}Sr in the final sample solutions are estimated to be 4.5% and 6%, respectively.

The Rust Geotech Laboratory analyzed one set of bottles once to verify the preparation process. The results obtained by Rust were within a range of 98% to 106% of the calculated concentration for ^{90}Sr which was within the calculated uncertainty. The results of the ^{89}Sr analysis were not within the estimated uncertainty, ranging from 114% to 171% of the calculated values.

Blanks and control samples were supplied by the individual laboratories. The study design specified that controls be approximately 100 pCi for ^{90}Sr and 20 pCi for ^{89}Sr.

Study Design

Each laboratory was supplied with seven 1,500-mL samples with activities of ^{89}Sr and ^{90}Sr ranging from 10 to 2,000 pCi/L. Aliquots from each sample were preconcentrated by each of the three preconcentration methods, purified on the ElChrom Sr resin column and counted by either Cerenkov counting (two laboratories) or gas proportional counting (four laboratories). The procedure was performed in duplicate for each preconcentration method and for each sample concentration. The procedure was repeated on a second set of duplicates on a different day. The laboratories were instructed to run a control and a blank with each set of seven samples; however, half of the laboratories ran only one set of controls and blanks with each day's run. Each laboratory was provided with forms on which to record results and a questionnaire on which to evaluate the method, including the written procedure, compared to the laboratory's currently used procedures.

Results

The study data were initially analyzed following American Society for Testing and Materials (ASTM) guidelines [9]. Following the initial analysis, additional statistical tests were performed.

Outliers
The data from Laboratory 5 were not included in the analysis for this study because their ^{90}Sr data were 2 to 2.5 times both the values reported by the other laboratories and the reference values of the samples, and because multiple procedural errors were identified in the course of trying to determine the source of the discrepancies.

The remaining data were tested for normality and outliers by the Wilk-Shapiro W statistic and kurtosis methods. On the basis of these methods, 16 reported values were determined to be outliers and were not included in further data analysis.

Bias

In general, the laboratories produced positive biases for ^{89}Sr, and these biases were large. Specifically, the relative absolute bias percentages for the three preconcentration methods ranged from 2 to 129% with a mean of 62% for cation exchange; from 6 to 207% with a mean of 78.5% for calcium carbonate precipitation; and from 1 to 87% with a mean of 37.8% for calcium phosphate precipitation. Although a plot of the data does not indicate

a linear relationship between the bias and the concentration of the sample, the relative absolute biases are smaller for the two samples with the highest concentrations.

Biases for ^{90}Sr are negative for all preconcentration methods and samples; however these biases are generally small. The relative absolute bias percentages for the ^{90}Sr measurements ranged from 8 to 11% with a mean of 8.9% for cation exchange; from 5 to 11% with a mean of 6.6% for calcium carbonate precipitation; and from 4 to 10% with a mean of 7.3% for calcium phosphate precipitation. The plot of the biases versus the reference values for the ^{90}Sr indicates that the biases are linearly dependent on the concentrations.

Repeatability and Reproducibility

As described by the ASTM, repeatability is a measure of precision within a laboratory and reproducibility is a measure of the variability of results between different laboratories. Both the repeatability and the reproducibility standard deviations for the ^{89}Sr are generally large and are not linearly dependent on the reference value. The relative repeatability and reproducibility percentage ranges for ^{89}Sr for each of the preconcentration methods are listed in Table 1.

Table 1. Repeatability and Reproducibility Standard Deviation Percentages for ^{89}Sr.

Preconcentration Method	^{89}Sr Repeatability (%)			^{89}Sr Reproducibility (%)		
	Low	High	Mean	Low	High	Mean
Cation exchange	15	101	52.1	30	168	83.1
Calcium carbonate	16	287	94.8	31	307	123.3
Calcium phosphate	8	66	40.2	27	126	68.5

For ^{90}Sr, the graphs of the repeatabilities and the reproducibilities versus the reference values, to some degree, reveal a linear relationship; however, both the repeatability standard deviation and the reproducibility standard deviation are in general small, as revealed in the table of relative percentage ranges, shown in Table 2.

Table 2. Repeatability and Reproducibility Standard Deviation Percentages for ^{90}Sr.

Preconcentration Method	^{90}Sr Repeatability (%)			^{90}Sr Reproducibility (%)		
	Low	High	Mean	Low	High	Mean
Cation exchange	4	14	8.6	11	20	14.9
Calcium carbonate	5	12	8.4	10	27	14.0
Calcium phosphate	5	15	8.6	12	22	16.6

Consistency Statistics h and k

The h statistic for consistency between laboratories shows that, for both ^{89}Sr and ^{90}Sr, the measurements from an individual laboratory tended to be either consistently high or consistently low relative to the measurements from all laboratories. This was much more apparent in the measurements of ^{90}Sr than it was for ^{89}Sr.

The k statistic for consistency within a laboratory shows problems for individual laboratories for single samples. No laboratory had a pattern of inconsistency for the study.

ANOVA

Three possible factors that could influence the outcome of the measurements are the preconcentration method, the laboratory performing the analysis, and whether the analyses were performed on the same day or on different days. A fourth factor, the counting method used, is a potential source of variation. This variable is not addressed because the data collected from this study are insufficient for such analysis.

Of the three variables analyzed, the laboratory performing the analysis was the greatest source of variation. The difference among laboratories is significant at 1% for almost all combinations of analytes and samples. The effect of performing the analysis on different days was significant at the 1% level for 5 of 14 combinations of analytes and samples; however, this statistic also includes interlaboratory variability. The preconcentration method was not significant at the 1% level for any combination of analyte and sample.

Concordance

Lin [7,8] developed and studied an index called the concordance correlation coefficient to assess the agreement between two readings. When a particular preconcentration method is used with a particular analyte, this index evaluates the agreement between the observed values and the reference values, how far the best-fit line deviates from the 45° line (measure of accuracy), and how far each observation deviates from the best-fit line (measure of precision).

The following observations were made from this analysis:

- The concordance statistics indicate that the agreement between the observed values and the reference values for ^{89}Sr are unsatisfactory for all three preconcentration methods. Although not apparent through ANOVA tests, however, the agreement for calcium phosphate precipitation is better than the agreement for either calcium carbonate precipitation or cation exchange.

- The agreement between the observed values and the reference values for ^{90}Sr are very satisfactory, and no significant difference is observed among the three preconcentration methods.

Testing the True Values

The standard Student's t statistic was applied to a given analyte, sample, and preconcentration method to test for the reference values of the sample being the true values, under the assumption that the observed values form normal random samples. The

reference values for the ^{90}Sr are supported by this test, however, such a conclusion can not be reached in regards to the ^{89}Sr.

Remarks

Two of the laboratories indicated on their questionnaires that they are currently using the Sr resin columns. The consensus of all of the laboratories regarding the three preconcentration methods was mixed, depending on the amount of difficulty encountered and the comparison to the method they currently use. However, the laboratories did indicate that although the column itself is more expensive, the saving in labor and in waste generated and the improved quality of the results make this a preferred method.

Conclusions

The Eichrom Sr resin column isolates elemental strontium. ^{89}Sr and ^{90}Sr were used to validate this method. The variability in the ^{89}Sr data and their lack of correlation with the reference values of the samples make it an ineffective measure of the validity of this method. The repeatability and reproducibility of the data obtained from the ^{90}Sr, however, demonstrate that the method is effective for isolating strontium.

The ^{89}Sr data generated from this study are extremely imprecise. We believe, but cannot definitively prove, that the imprecision was a result of measurement problems. Although three measurement methods are recommended in the procedure, only two of these methods were used in the study: Cerenkov counting (two laboratories) and gas proportional counting (three laboratories). This gave us insufficient data to analyze the effects of the measurement methods on the results. However, since the chemistry involves an elemental separation of strontium, it could not generate accurate ^{90}Sr data if the chemical procedure were inadequate. Therefore, this further supports the hypothesis that the poor ^{89}Sr data are a result of the measurement specific to this nuclide.

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