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Rapid Method for Determination of Radiostrontium in Emergency Milk Samples

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Abstract

A new rapid separation method for radiostrontium in emergency milk samples was developed at the Savannah River Site (SRS) Environmental Bioassay Laboratory (Aiken, SC, USA) that will allow rapid separation and measurement of Sr-90 within 8 hours. The new method uses calcium phosphate precipitation, nitric acid dissolution of the precipitate to coagulate residual fat/proteins and a rapid strontium separation using Sr Resin (Eichrom Technologies, Darien, IL, USA) with vacuum-assisted flow rates. The method is much faster than previous method that use calcination or cation exchange pretreatment, has excellent chemical recovery, and effectively removes beta interferences. When a 100 ml sample aliquot is used, the method has a detection limit of 0.5 Bq/L, well below generic emergency action levels.

Introduction

There is an increasing need to develop faster analytical methods for emergency response, including rapid determination of Sr-90 in milk.[1,2,3] In a radiological emergency such as nuclear power plant accidents, fallout from nuclear detonation or a radiological dispersive device, rapid measurement of Sr-90 in a variety of environmental and bioassay matrices is essential. Milk ingestion is a substantial path for radiostrontium intake into the

human body, especially for infants [4] and milk contamination level gives an indication of the radiostrontium deposition over a wide area. [5]

Rapid methods for actinides and radiostrontium in emergency water and urine samples have been developed by the Savannah River Site (SRS) Environmental Bioassay laboratory to perform measurements in less than 8 hours. [6, 7] There is a need for a faster method to measure radiostrontium in milk as well. There are variety of methods available to measure radiostrontium in milk, including radiometric and mass spectrometric methods. Inductively-couple mass spectrometry methods have been used to measure Sr-90, but these techniques suffer to some extent by isobaric interference of Z-90 and abundance sensitivity, i.e. the tail from stable strontium (m/z=88) present in the sample on m/z=90. [8] Sr-90 ($T_{½}$ = 28.5 years) and its daughter Y-90 ($T_{½}$ = 64.4 hours) are beta emitters that must be separated from the sample matrix prior to measurement. The classical separation scheme of Harley [9] is difficult and time-consuming. Other methods to separate Sr-90 have been proposed that include cation exchange collection followed by extraction chromatography. Cation exchange collection methods have sometimes required long contact times and relatively large volumes of strong acid eluant (300-400 ml) to remove the strontium from the cation resin, which in turn typically needs to be evaporated prior to further processing, adding significant analysis time. In some cases, cation exchange separation has been enhanced by adding a bicyclic polyether cryptand such as cryptand 222 to the cation resin to reduce contact times. Tait [10] reported a method that uses cation exchange collection enhanced with cryptand 222, evaporation and Sr Resin that takes 24 hours. Tovedal [11] has used very small volume milk samples to determine Sr-90 by measuring Y-90 by Cerenkov counting after separation and in-growth to meet a generic

action level of 100 Bq /L in 24 hours. The method uses microwave digestion to digest 5 ml sample aliquots, followed by extraction using Sr Resin (Eichrom Technologies, Darien, IL, USA), obtaining a detection limit of 50 Bq ^{90} Sr/L.

A new rapid separation method for radiostrontium in emergency milk samples has also been developed at the SRS Environmental Bioassay Laboratory (Aiken, SC, USA) that will allow rapid separation and measurement of radiostrontium within 8 hours, faster than previously reported methods. The method has some flexibility with regard to sample aliquot size; however, when a 100 ml sample aliquot is used, the method has a detection limit of 0.5 Bq/L. The new method uses calcium phosphate precipitation, nitric acid dissolution of the precipitate that coagulates residual fat/proteins and strontium separation using Sr Resin (Eichrom Technologies, Darien, IL, USA) with vacuum-assisted flow rates. The effectiveness of Sr-Resin to rapidly separate strontium from beta interferences is well-documented.[12,13]

Experimental

Reagents

The resin employed in this work is Sr-Resin ® (4, 4', (5') di-t-butylcyclohexane-18-crown-6), available from Eichrom Technologies, Inc., (Darien, Illinois, USA). Nitric acid was prepared from reagent-grade acids (Fisher Scientific, Inc.). All water was obtained from a Milli-Q2™ water purification system. All other materials were ACS reagent grade and were used as received. A solution of 20.95 mg/ml stable strontium was used to determine strontium carrier recovery. The strontium carrier solution was standardized gravimetrically using a strontium carbonate precipitation technique. An

aliquot containing 4.19 mg of Sr carrier solution was added to each sample. Sr-90 was obtained from Analytics, Inc. (Atlanta, GA, USA) and diluted to approximately 80 pCi/ml.

Procedures

Column preparation. Sr-Resin columns were obtained as cartridges containing both 2 ml and 1 ml of resin from Eichrom Technologies, Inc.. Small particle size (50-100 micron) resin was employed, along with a vacuum extraction system (Eichrom Technologies). Flow rates of 1 -2 ml/min were typically used.

Sample Preparation. Twelve samples of fresh whole milk from a dairy farm were analyzed. A 100 ml aliquot of each milk samples was aliquoted into a 225 ml centrifuge tube. Sr carrier (4.19 mg Sr) was added to each sample. Two samples were analyzed as blanks. Sr-90 standard was added to samples 3-12 such that three samples contained 0.57 Bq, three samples contained 1.47 Bq and four samples contained 0.286 Bq that was added by transferring a small volume of NIST (National Institute of Standards and Technology, Gaithersburg, MD, USA) water standard used in its emergency response exercise program (NIST Radiochemistry Intercomparison program). Fifty milliliters of water were also added to each tube to facilitate the phase separation since the cream content was so high (fat content ~8%). Two mL of 1.25M calcium nitrate and 5 mL of 3.2M ammonium hydrogen phosphate were added to each sample. The pH was adjusted to pH 10 with concentrated ammonium hydroxide using a phenolphthalein endpoint. The samples were centrifuged at 3500 rpm for 10 minutes. After discarding the supernate, twenty milliliters of 3M HNO_3 was added to each tube and mixed with the precipitate. The samples were

centrifuged at 3500 rpm for 10 minutes (much of the fat/protein coagulates in the bottom of the centrifuge tube) and the supernate containing the dissolved calcium phosphate precipitate was transferred to a 250 ml glass beaker. The beaker was placed on a hot plate at medium heat to evaporate the supernate, which contains a small amount of residual fat. The precipitate of coagulated fat/protein in the centrifuge tube was rinsed once with 10-15 mL of 3M HNO_3 and centrifuged at 3500 rpm for 10 minutes. The supernate was transferred to the same beaker containing the initial supernate solution and evaporated to dryness. Approximately 5 ml of 15.7M HNO_3 and 5 ml of 30 wt% hydrogen peroxide was added to each beaker and the samples were wet-ashed to dryness on the hot plate. The beakers were transferred to a large muffle furnace that was preheated to 550C and heated for 30-60 minutes. The beakers were removed and allowed to cool. Approximately 5 ml of 15.7M HNO_3 and 5 ml of 30 wt% hydrogen peroxide was added to each beaker and the samples were wet-ashed to dryness on the hot plate. The samples were redissolved in 5 ml of 15.7M HNO_3 and 5 ml of 2M $Al(NO_3)_3$, warming as needed on the hot plate.

Column separation. The sample solutions were loaded to 3 ml Sr resin cartridges (stacked 2 ml plus 1 ml cartridges) at approximately 1 drop per second, using vacuum. Each beaker was rinsed with 3 ml of 8M HNO_3 and this rinse was added to the column. The Sr Resin cartridges were rinsed with 15 mL of 8M HNO_3, 5 ml 3M HNO_3-0.05M oxalic acid, and 7 ml 8M HNO_3 respectively at 1-2 drops per second. The Sr-89/90 was stripped from the Sr Resin using 13 mL of 0.05M HNO_3 into 50 mL tubes at 1 drop per second. This solution was transferred to preweighed planchets and evaporated on a hot plate to dryness. A 2 mL volume of 8M HNO_3 was used to rinse each tube and then was transferred to each planchet and dried. The dried planchets were allowed to cool and then

were weighed to determine gravimetric carrier recovery. The planchets were counted by simultaneous gas proportional counting. Figure 1 shows the flow chart of the new emergency method, showing that a set of 12 samples can be analyzed in 8 hours. The initial aliquotting and calcium phosphate precipitation processing takes about 3 hours. A short furnace step to remove residual fat/protein takes less than 1 hour. The Sr Resin separation takes about 2.5 hours, including evaporation of purified solutions on planchets. The counting times tested were 20 minutes and 60 minutes. Figure 2 shows the initial calcium phosphate precipitate, which also includes a significant amount of protein/fat. In this particular case, the precipitate shown results from a larger 500 ml sample aliquot. Figure 3 shows the redissolved precipitate in 3M HNO_3 and the coagulated protein/ fat. Figure 4 shows the sample after wet-ashing and furnace steps have been completed, while Figure 5 shows the redissolved sample solution just prior to separation on Sr Resin.

Apparatus

Radiostrontium measurements were performed using a Tennelec LB 4100 gas proportional counter. Polycarbonate vacuum boxes with 24 positions and a rack to hold 50 ml plastic tubes were used.

Results and Discussion

Table 1 shows the individual ^{90}Sr results for a 20 minute count time. The average gravimetric recovery of stable strontium for 12 samples was 75.1% ± 17% (SD). The average difference from the ^{90}Sr reference value for the 10 spiked samples was 3.19%. The individual values agree well with the reference values, except for one sample that was

38% high. The method uncertainty for that sample was relatively high, however with k=3 uncertainty of 37%. When counted for 60 minutes, however, this sample did not exhibit a significant bias. For emergency response screening, the data quality would likely be sufficient, but if improved accuracy and precision were needed the samples could have been counted longer. The MDA (Minimum Detectable Activity) for a 100 ml sample aliquot and 20 minute count is 0.5 Bq/L, well below a generic emergency action level of 100 Bq/L.

Table 2 shows the individual ^{90}Sr results for a 60 minute count time. The average difference from the ^{90}Sr reference value for the 10 spiked samples was only 0.52%. The individual values agree well with the reference values, all differences were within the stated k=2 uncertainty (%).The MDA (Minimum Detectable Activity) for a 100 ml sample aliquot and 60 minute count is 0.15 Bq/L.

This method has also been applied in the SRS Environmental Bioassay Laboratory to routine milk samples for environmental monitoring purposes, using a 500 ml sample aliquot. The larger sample was split between two centrifuge tubes and later combined into a single tube. For a set of test data (N= 7), a spike level of 2.96 Bq ^{90}Sr added per 500 ml sample aliquot, a 30 minute count time, the average ^{90}Sr spike recovery was 93.0% ± 7% (SD). This demonstrates that same separation chemistry used in the ^{90}Sr emergency method can be adapted for used for analysis of routine milk samples.

If individual Sr-89 and Sr-90 results are required, a second count measured after 7-10 days can be used to differentiate Sr-89 and Sr-90. There are also Čerenkov counting techniques for more rapid determination of Sr-89 and Sr-90. [14] Although regeneration and reuse of Sr Resin cartridges has been reported [15], this is not done in the SRS

Environmental Laboratory to reduce any chance of cross-contamination or degradation of resin performance.

Conclusions

The new radiostrontium in milk method developed in the SRS Environmental Bioassay Laboratory is a rapid method that can be used for the rapid measurement of radiostrontium in emergency milk samples. The method can also be applied for routine environmental monitoring using larger sample aliquots. The calcium phosphate precipitation and acidification step to remove residual fat and protein is an effective way to rapidly remove sample matrix interferences. The MDA level of 0.5 Bq/L for a 20 minute count on a 100 ml sample aliquot provides adequate detection of radiostrontium to meet generic emergency response action levels.

Acknowledgment

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Table Captions

Table 1. Performance of New ^{90} Sr Emergency Method - 20 minute Count

Table 2. Performance of New ^{90} Sr Emergency Method - 60 minute Count

Figure Captions

Figure 1 Flow Chart of New Radiostrontium Emergency Method

Figure 2 Calcium Phosphate Precipitate from Milk

Figure 3 Redissolved Calcium Phosphate Precipitate and Coagulated Fat/Protein

Figure 4 Wet-Ashed Sample Ready for Redissolution and Column Extraction

Figure 5 Clear Dissolved Milk Sample in 10 ml Volume in 8M HNO_3-1M $Al(NO_3)_3$

Table 1. Performance of New Radiostrontium Emergency Method - 20 minute Count

^{90}Sr Added (Bq/L)	^{90}Sr Measured (Bq/L)	Uncertainty (%, K=-2)	Difference (%)
0	0.26	98.9	N/A
0	0.34	81.9	N/A
2.86	2.66	24.1	-7.0
2.86	3.96	24.7	38
2.86	3.31	20.2	15.7
2.86	2.67	18.7	-6.6
5.70	6.11	16.7	7.2
5.70	5.71	13.1	0.2
5.70	5.16	13.9	-9.5
14.3	12.8	9.1	-11
14.3	15.2	8.5	6.3
14.3	14.1	8.6	-1.4
		Average	3.19

Table 2. Performance of New Radiostrontium Emergency Method - 60 minute Count

^{90}Sr Added (Bq/L)	^{90}Sr Measured (Bq/L)	Uncertainty (%, K=-2)	Difference (%)
0	0.11	130	N/A
0	0.27	59	N/A
2.86	3.09	13.2	8.0
2.86	3.11	16.7	8.7
2.86	2.67	13.6	-6.6
2.86	2.67	11.3	-6.6
5.70	5.85	10.4	2.6
5.70	5.75	8.3	0.9
5.70	6.04	8.2	5.9
14.3	13.6	6.1	-4.9
14.3	14.0	6.1	-2.1
14.3	14.2	6.1	-0.7
		Average	0.52

Figure 1 FlowChart of New Radiostrontium Emergency Method

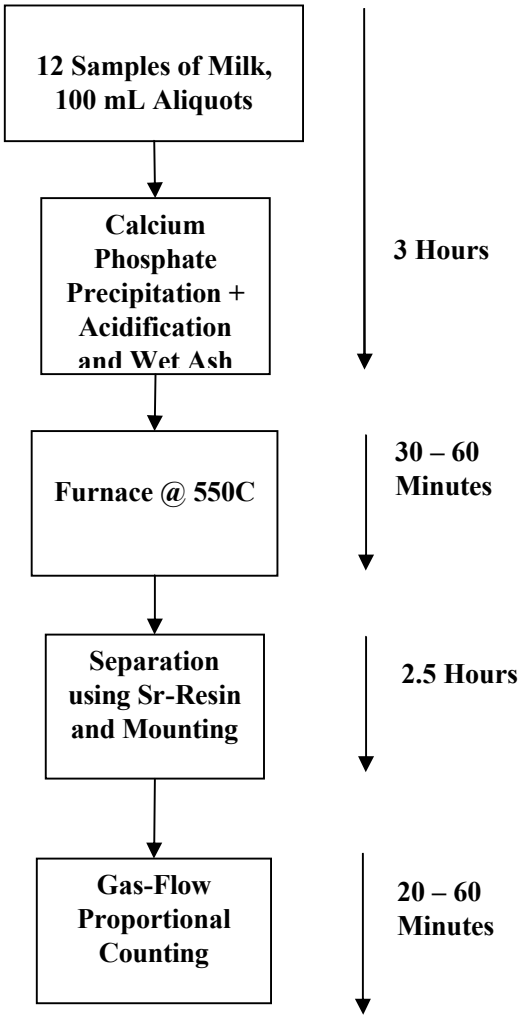

Figure 2 Calcium Phosphate Precipitate from Milk

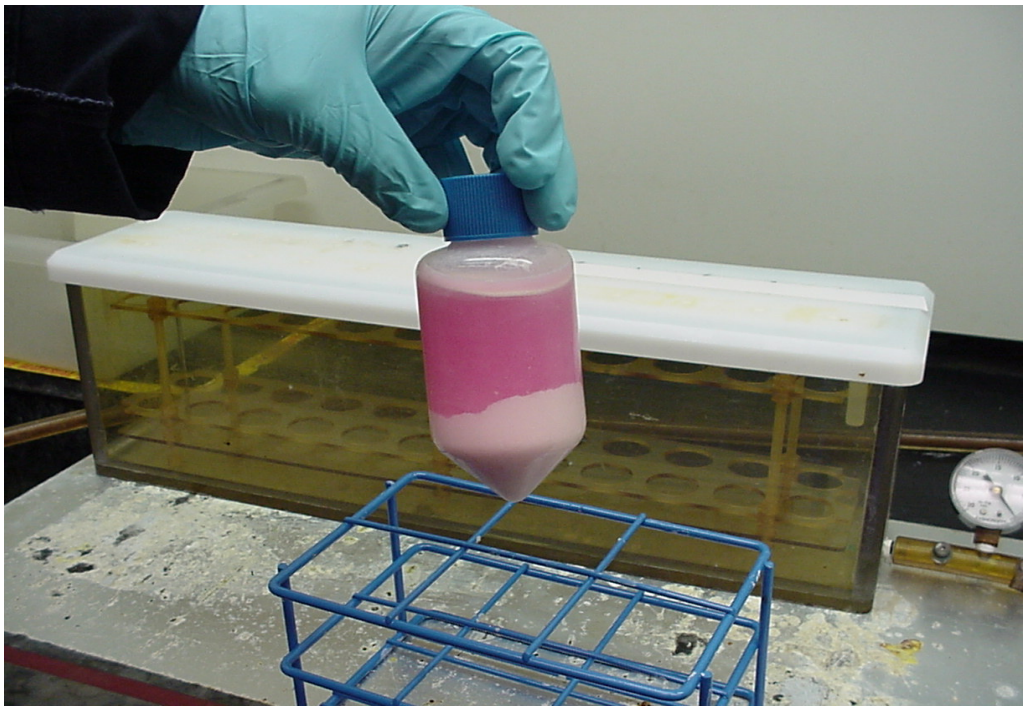

Figure 3 Redissolved Calcium Phosphate Precipitate and Coagulated Fat/Protein

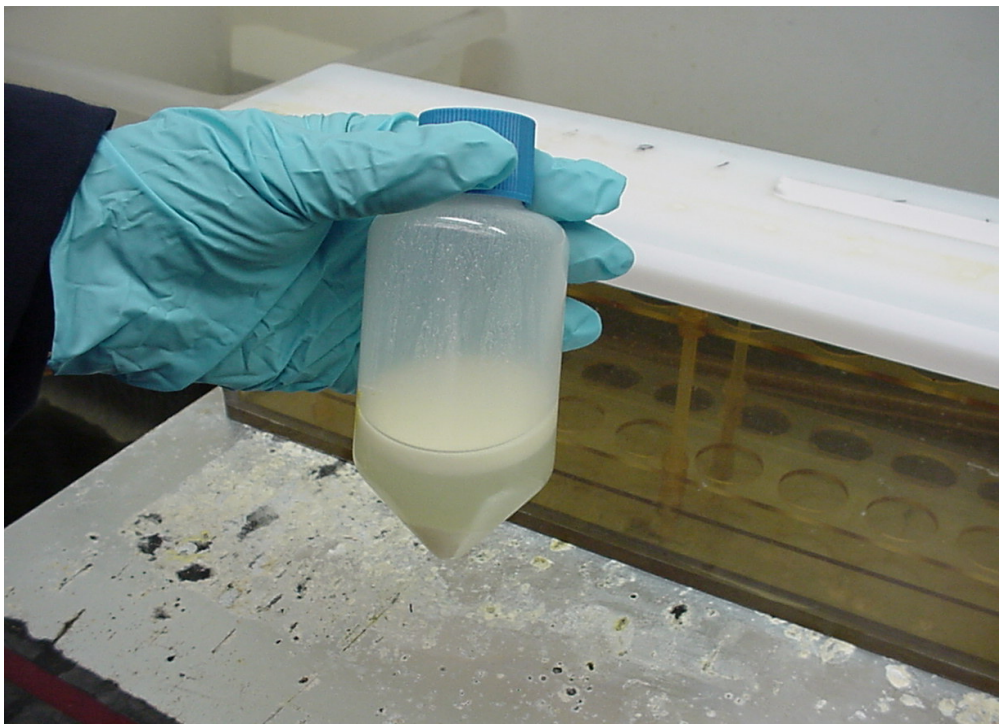

Figure 4 Wet-Ashed Sample Ready for Redissolution and Column Extraction

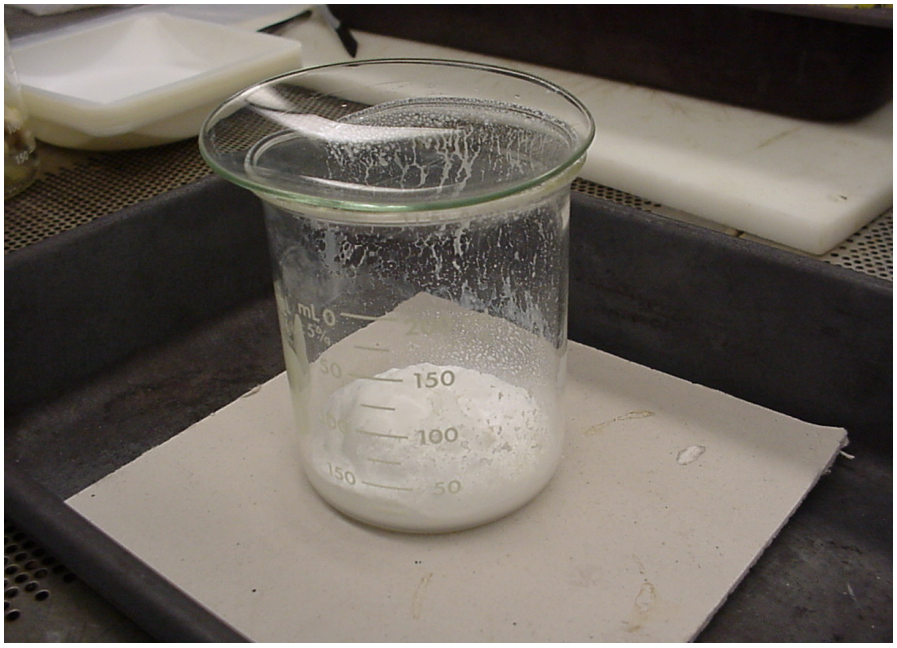

Figure 5 Clear Dissolved Milk Sample in 10 ml Volume in 8M HNO_3-1M $Al(NO_3)_3$