

RE-USE OF Sr CHROMATOGRAPHY RESIN IN LARGE DIAMETER COLUMNS

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Abstract

The details of a new approach to re-use of Sr resin are described. This new approach utilizes larger columns so that up to 20 mg of Sr carrier can be used in radiostrontium analysis procedures. The increased capacity and use of larger amounts of carrier improves the accuracy of gravimetric yield determinations and reduces the bias caused by small amounts of stable Sr in environmental samples. Elution chromatograms for large capacity columns are presented, and cross-contamination data is discussed.

Introduction

One of the limitations to the use of Sr Resin™ for the determination of Sr isotopes is the limited capacity of the resin. This limits the amount of Sr carrier which can be used in the procedure. When a gravimetric method is employed for yield determination, unacceptably large uncertainties can sometimes result. These uncertainties are the result of the difficulty in complete rinsing of a filtered precipitate. In addition, there can be considerable difficulty in bringing the filter to constant weight prior to filtration of the sample. When large filters are used to maximize counting efficiency, the problem becomes even worse. A 2 mg uncertainty in the weight of the precipitate amounts to a relative standard deviation of 24% when 5 mg of Sr is precipitated as SrCO₃. When the yield is less than 100%, the uncertainty becomes even larger. To minimize the impact of these problems on the accuracy of the yield determination, it would be desirable to use a larger amount of carrier.

Another problem that occurs with the use of small amounts of carrier is the effect of stable Sr in the sample. Of course stable Sr in a sample can be determined separately and the appropriate correction can be made. However, this can increase the time required for the determination, and it requires the use of atomic absorption or ICP emission spectroscopy instrumentation which may not be readily accessible to some radiochemistry laboratories. In general, however, the amount of stable Sr present in small environmental samples could be insignificant if a large amount of carrier, e. g., 20 mg could be used.

A Sr column of larger capacity would solve both of these problems, but it would also increase the cost of doing the analysis, since four times as much resin would be required. Unless the resin columns could be reused, the analysis could not be competitively priced. Environmental Physics, Inc. and Florida State University have undertaken a study in the feasibility of reusing large columns of Sr resin.

Experimental

In order to accommodate 20 mg of Sr carrier and still have some reserve capacity, 3 grams of resin was used. This is approximately 4 times the amount of resin contained in the pre-packed Sr columns provided by EICrom. The resin was 80-160 μ material. The columns were plastic, 1.6 cm ID \times 15.5 cm, obtained from Environmental Express. The flow rates with these columns was faster than with the pre-packed columns. The average flow rate starting with 70 mL of eluent in the reservoir was about 3 mL/minute.

The first set of experiments was done at FSU. The first step of the process was to determine the elution profile so that proper elution volumes could be established. The column was conditioned with 10 mL of 8M HNO₃. The sample load solution was 20 mL of 8M HNO₃ containing 20 mg of Sr and ~220,000 dpm of Sr-85 tracer. The column was rinsed with 15 mL of 8M HNO₃, and Sr was eluted with 40 mL of 0.05M HNO₃. The load, rinse, and eluent solutions were collected in 1-mL increments and counted in a NaI well detector. From the counting results, the elution profile was constructed. Blank solutions contained 20 mg of Sr carrier, but no Sr-85. A blank was then run through the column, followed by eight sets of consecutive sample-blank pairs.

In the fifth sample-blank set the Sr-85 recovery dropped to 94%. Sr-85 recoveries for sets 6-9 continued to decrease, reaching 90% for the ninth sample. A second elution profile was obtained at this point. The column had now been used 18 times. The second profile suggested that quantitative recovery of Sr could be achieved by increasing the eluent volume from 40 mL to 70 mL. Throughout the remainder of the experiments, 70 mL was established as the elution volume, and the load solution and rinse were changed to 3-4M HNO₃.

Results

The next phase of the experiment studied residual column contamination. Sr-85 recovery was determined for samples, and residual Sr-85 was determined in blanks. Residual Sr-85 in the blanks from the columns used in the elution profiles gradually increased, rising to almost 10%. This confirmed the elution curve data that the Sr elution volume should be increased, and we also considered other eluents.

Using 0.1M HClO₄ instead of 0.05M HNO₃, Sr-85 recovery for the first sample was less than 100%, and recoveries continued to decrease with subsequent samples. Since K⁺ and NH₄⁺ also compete with Sr for resin sites, the next approach was to see if addition of potassium would enhance Sr elution.

A new column was prepared, and the next eluent chosen was 0.05M HNO₃ - 0.1M KNO₃. Using this eluent, Sr-85 recovery in samples seemed to improve slightly. Figure 1 shows the chronology of samples and blanks analyzed. The first five runs were spiked samples. No blanks were run until Sample 6. We wanted to see if there was a tendency for residual Sr to build up. Residual Sr in the blanks was variable, ranging from 0 to 1%. A small amount, less than 1%, of the Sr-85 appeared in the load/rinse of Sample 8, which was a blank. Normally, this would indicate breakthrough had occurred. Since no Sr-85 was added to this sample, the activity had to be due to residual Sr which had worked its way to the bottom of the column. Sr-85 was found again in the load/rinse from Sample 12, which was also a blank. Breakthrough increased in all the subsequent samples. The subsequent blank had only a trace of Sr-85. We concluded,

therefore, that the addition of KNO_3 might be beneficial since we were able to maintain 100% Sr-85 recovery for the first 11 runs.

An interesting blank observation occurred with a column that was filled with DI water and left standing over a weekend. Significant Sr-85 was found in the effluent. This finding led to soaking the resin between uses. We also started the practice of following the 70 mL 0.05M HNO_3 elution with a 70-mL water rinse. With a 3-day soak between uses, residual Sr-85 decreased to 0.1%.

The final experiments were conducted at EPI. The elution profiles were repeated to ensure that the process could be duplicated, this time using Sr-89 as a tracer. Three series of sample-blank sets were run. Series 1, performed in duplicate, consisted of five runs of a sample of Sr-89, followed by a blank the next day. Series 2, also performed in duplicate, consisted of five runs of a sample, followed by a blank in 48 hours. Series 3, also performed in duplicate, consisted of 10 runs of a sample, followed by a blank in 72 hours. Because of weekend interruptions, the actual results obtained were 8 observations with a 1-day soak, 8 observations with a 2-day soak, 10 observations with a 3-day soak, and 4 observations with a 4-day soak. The results are shown in the table below.

Table 1

RESIDUAL ACTIVITY IN "SOAKED" RESIN

"Soak" Period	Residual Activity Range, %, of Original Spike	Number of Experiments	Mean, %
1 day	0.08 - 0.91	8	0.44 ± 0.28
2 days	0 - 0.52	8	0.34 ± 0.21
3 days	0.13 - 0.66	10	0.32 ± 0.15
4 days	0.28 - 0.36	4	0.33 ± 0.03

It is clear from the above table that a soak of at least 3 days should accompany any reuse of Sr resin. We would therefore expect residual Sr levels in the resin to be no greater than 0.3% of the activity of the previous sample.

The source of the used resin for these experiments was obtained from a large container of material that had been used once. At the conclusion of an analysis at EPI, the spent resin is extruded from the column into a large container. This material represents a wide range of matrices and sample activities. So another experiment was conducted to determine if the residual Sr problem was limited to used resin. Two columns were prepared. One contained new resin, and the other contained used material.

Five sets of sample-blank pairs using Sr-89 tracer were run on each column. Sr-89 recovery was determined by gas-flow counter using a gravimetric yield determination. After the 3-day soak, residual Sr was eluted with 70 mL of water prior to conditioning the column for the

next run. These effluents, unfortunately, were not analyzed. The eluent used for samples and blanks did not contain KNO_3 because of some minor problems associated with the gravimetric yield determination in the presence of so much salt. Sr-89 recovery for all samples was 100%, and the blank residual Sr-89 levels are presented in Table 2.

Table 2

RESIDUAL ACTIVITY IN NEW AND USED RESIN					
% OF ORIGINAL SPIKE					
Sample	1	2	3	4	5
New Resin	0.57	1.26	0.48	0.08	0.10
Used Resin	0.41	0.56	0.65	0.10	0.07
ΔT , days	3	3	3	4	3

The blanks from Sample 1 were repeatedly over the next 30 days to verify by half-life that the activity was due to Sr-89. The half-lives calculated were 79 days and 90 days, respectively, for the new and used resins.

With these data in mind, we began the final phase of the experiments. EPA cross-check samples were chosen as test samples because water is a simple matrix and would not complicate the analysis to the point where it would be difficult to assess the performance of the resin. The analytical procedure consisted of SrCO_3 precipitation to isolate Sr for column loading. The Sr effluent was stored for 7-10 days for Y-90 ingrowth. Yttrium carrier was added, and Y-90 was separated and purified by several precipitations with ammonium hydroxide, followed by final precipitation as oxalate. Counting was done by gas-flow proportional counter. The analysis results are summarized in Table 3.

Conclusions

Independent experiments at FSU and EPI have demonstrated that the residual Sr in used Sr resin is less than 1% of the sample amount. Similar results have been presented at previous Bioassay Meetings. In addition, we have shown that columns could be used at least 10 times with satisfactory performance before significant recovery losses occur. Because of the agreement between the results of the soak experiments and the new-old resin study, the expected residual Sr should be less than 1%. However, the data presented in Table 3 is an apparent contradiction.

The most troublesome aspect of the EPA cross-check results is the residual Sr. The blanks analyzed with the EPA samples are well above 1%. In fact, the residual Sr in Blank 2 which followed Sample 1 in chronology, is 10%. This is difficult to explain in view of the fact that the minimum level of spike activity used in experiments at EPI was always greater than 40

times the activity in the EPA samples, and in the FSU experiment, the spike activity was almost 100,000 times greater.

Table 3

EPA SAMPLE RESULTS, pCi/L				
SAMPLE	RESULT	EPA VALUE	EPI/EPA	ACCEPTED RANGE
#1 - 10/17/95	18.7	10	1.87	1.3 - 18.7
	18.2		1.82	1.3 - 18.2
Blank #2	1.1			
	1.7			
	1.2			
#3 - 1/23/96	6.1	5	1.22	0 - 13.7
#4 - 4/16/96	14.6	16	0.91	7.3 - 24.7
#5 - 1/23/96	4.7	5	0.94	0 - 13.7
Blank #6	0.48			
	1.12			

A possible explanation for residual contamination in general is column kinetics. The columns used were chosen for the simple reason that they were on hand. A column of smaller diameter would have produced slower flow rates, which would allow more equilibration time between resin and eluent. If that were not the case, the soaking periods would not have reduced the residual contamination. More experiments with smaller diameter columns is being planned. It is important to determine the reason for the variation in blank residuals.

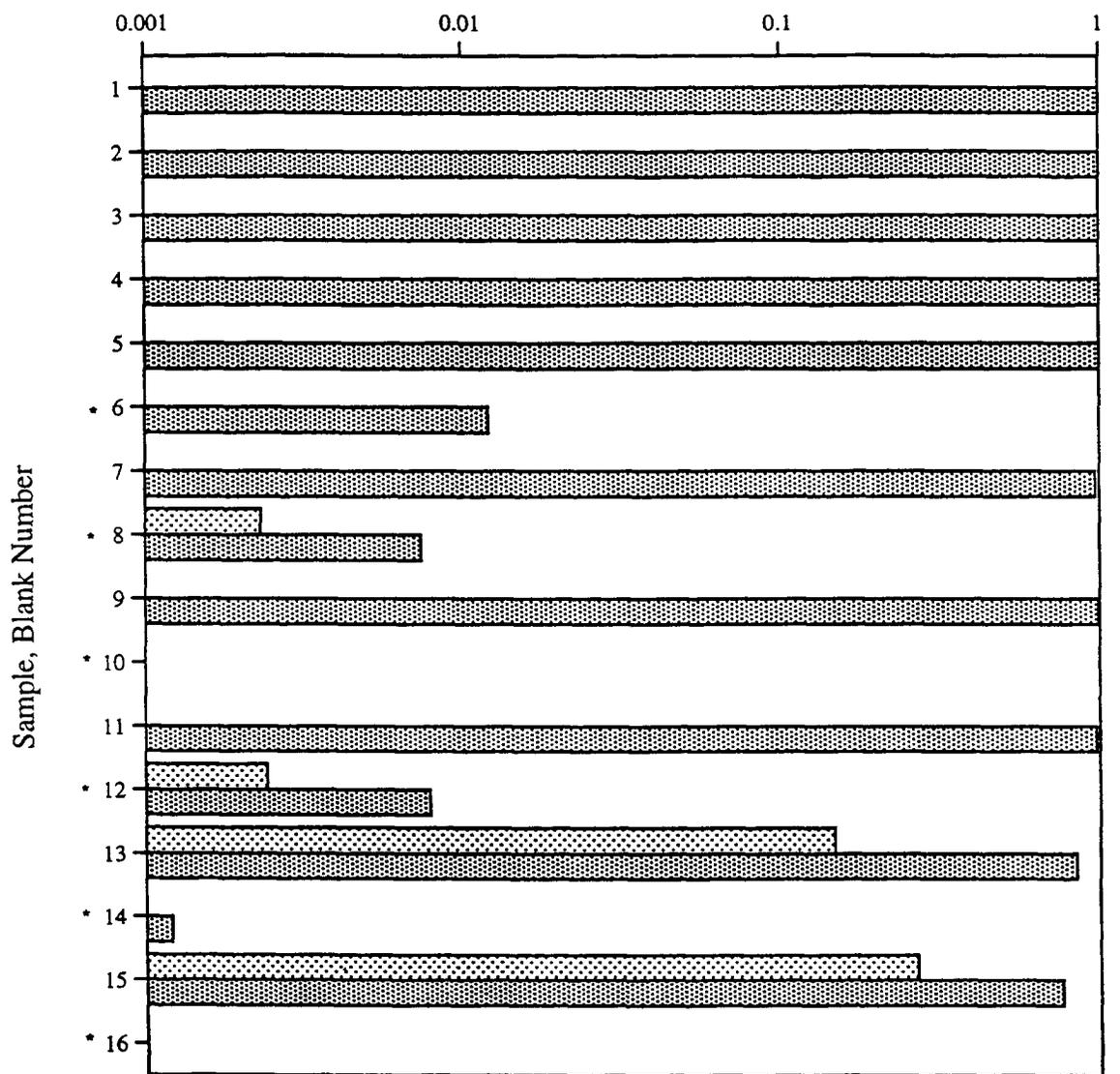
The quantitative data from the limited number of intercomparison samples analyzed is encouraging. The first sample was at the 3-sigma tolerance limit, and no explanation has been found for the disappointing performance. The yttrium oxalate precipitate was recounted after 3 days to verify the half-life.

The calculated half-life values for the experiment using new and used resin did not agree very well with the theoretical value of 50.55 days. These blanks were counted for 200 minutes, but due to the low activity, only 600-1000 net counts were observed. Predicting a half-life from such data is not expected to give precise results. However, the data do indicate that the residual activity is real and not due to counter background anomaly.

We believe these results are promising. However, the issue of resin reuse must be approached with caution. In addition to solving the problem with residual contamination, we also need to rigorously investigate whether or not complex sample matrices might increase the rate at which the resin is degraded.

Figure 1

Sample, Blank/Reference Ratio



*blanks

Load & Rinse
Elution