Towards a Method of Rapid Extraction of Strontium-90 from Urine: Urine Pretreatment and Alkali Metal Removal

Nuclear Engineering Division

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by

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ABSTRACT

A technical program to support the Centers of Disease Control and Prevention is being developed to provide an analytical method for rapid extraction of Sr-90 from urine, with the intent of assessing the general population's exposure during an emergency response to a radiological terrorist event. Results are presented on the progress in urine sample preparation and chemical separation steps that provide an accurate and quantitative detection of Sr-90 based upon an automated column separation sequence and a liquid scintillation assay. Batch extractions were used to evaluate the urine pretreatment and the column separation efficiency and loading capacity based upon commercial, extractant-loaded resins. An efficient pretreatment process for decolorizing and removing organics from urine without measurable loss of radiostrontium from the sample was demonstrated. In addition, the Diphonix® resin shows promise for the removal of high concentrations of common strontium interferents in urine as a first separation step for Sr-90 analysis.

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1. Introduction

An analytical method for the rapid extraction of Sr-90 from urine is being developed for the evaluation of individuals contaminated with radionuclides from a radiological terrorist event. This method will allow rapid evaluation and screening of individuals for possible exposure to Sr-90 by a critical medical management team and will allow contaminated individuals to be administered chemical countermeasures in the critical time frame after initial exposure. The method being developed will minimize the amount of urine for Sr-90 detection and will allow quantification at levels corresponding to U.S. NRC recommended annual limits of intake (ALI) for exposure to Sr-90 [1].

Current methods used for determination of Sr-90 in urine involve various concentration and separations steps [2-5], which are tedious and time-consuming and require a skilled technician. These steps have been employed to obtain quantitative recovery of strontium from urine and to minimize the detrimental effects of numerous interferences in the separation of strontium from urine. In an effort to speed up strontium separation and detection, we have examined various separation schemes to develop a simple and robust process. Normal human urine consists of ions (sodium, potassium, calcium, etc.) and organic molecules (urea, creatinine, uric acid, and smaller amounts of carbohydrates, enzymes, fatty acids, hormones, pigments, mucins, etc.). The composition of urine can vary greatly between subjects and is highly dependent upon diet. A certified human urine reference material is reported to have elemental concentrations of some ions that interfere with strontium separation: 0.14 M Na⁺, 0.034 M K⁺, and 0.0048 M Ca²⁺ [6]. These concentrations are high compared to the trace quantities of strontium required for the proposed separations.

The initial step in our process employs acidification of the urine with the intent of destroying any existing strontium complexes in urine and maximizing complexation onto extractant-loaded particles. Next, the method will exploit Sr-90 pre-concentration and separation technologies to allow analysis and detection from urine matrix interferences. The goal of these separations would allow triage decisions to be made based upon low limits of quantitation for potentially exposed patients. Detection of Sr-90 concentrations at greater than 10 times the ALI for exposure to Sr-90 would trigger patient treatment. However, detection of Sr-90 quantities below 1 ALI with confidence would be necessary for release of patients without treatment.

2. Urine Pretreatment

Human urine contains organic substances (*i.e.*, creatinine, urea, and bilirubin) whose presence can lead to fouling of extraction chromatographic media, excessive back pressure, and poor separation. Bilirubin is a metabolite of heme, is excreted in bile and urine, and is responsible for much of the yellow color observed in mammalian urine. Colored compounds such as bilirubin can be strong fluorescence/color quenchers in liquid scintillation analysis (LSA) of urine samples, diminishing counting efficiency. Removal or reduction of these interferences will improve the minimum detectable activity of the LSA method.

Achieving high recovery of radiostrontium requires minimal losses of analyte from the steps that precede the extraction. Work by Sadi et al. [7] has demonstrated that acidification is necessary for the decolorization of urine. These authors also found significant losses of Sr-90 on charcoal (50%) from 1% hydrochloric acid, in contrast to quantitative recovery of Sr-90 on Eichrom's pre-filter material. Our initial flow diagram for the urine pretreatment was ambiguous as to the order of use of Sr resin and Diphonix ion exchange resin in the sample stream. In either case, use of nitric acid or methane sulfonic acid (MSA) provides the flexibility for introduction of the sample stream to a variety of extraction chromatographic media, and subsequent LSA.

To evaluate the reduction of interfering organic substances in human urine and the extent of strontium lost in this process, Sr-85 spiked urine was treated with either concentrated nitric acid or neat MSA, and was contacted with activated charcoal or Amberlite XAD-7 prefilter beads (100-120 mesh). All samples were treated in a weight-to-volume ratio of 1:100. A single lot of normal human urine with a dark yellow color was used. Color and consistency were evaluated as a qualitative measure of organics removal. Strontium-85 was employed instead of Sr-90 to facilitate analyses during these development studies. Gamma count rates were used for controls and samples to calculate the recovery of Sr-85 for each acid concentration shown in Table 1. The observed colors upon acidification and after sustained contact with XAD-7 are listed in Tables 2 and 3, respectively. All samples treated with charcoal were immediately decolorized upon first contact and settling of the charcoal. The XAD-7 beads were much slower in uptake of color, reaching apparent equilibrium after repeated 1-2 min of vigorous mixing and standing for 30 min twice. All treated samples were clear aqueous solutions with no emulsion or bubble formation.

Table 1: Sr-85 Recovery from Urine Decolorizing Agents - Charcoal and Amberlite XAD-7

[Acid]	HNO ₃ /Charcoal % Recovery	Relative Uncertainty	MSA/Charcoal % Recovery	Relative Uncertainty
0.001 M	87.2%	2.3%	91.2%	2.0%
0.01 M	96.0%	2.2%	93.3%	1.0%
0.1 M	98.4%	2.1%	96.3%	1.9%
1 M	97.0%	2.3%	99.4%	1.6%
4 M	98.0%	2.6%	98.8%	2.2%
8 M	98.2%	1.8%		
[Acid]	HNO ₃ /XAD-7 % Recovery	Relative Uncertainty	MSA/XAD-7 % Recovery	Relative Uncertainty
0.001 M	99.1%	1.2%	114%	1.6%
0.01 M	98.3%	2.3%	100%	2.4%
0.1 M	97.3%	5.6%	97.2%	1.5%
1 M	98.5%	1.6%	98.8%	3.2%
4 M	99.3%	1.1%	99.3%	2.0%
8 M	99.3%	1.6%		

Table 2: Observations of Color Following Acidification of Urine

[HNO ₃], M	Color of Liquid	[MSA], M	Color of Liquid
0.001	Light Yellow	0.001	Light Yellow
0.01	Light Yellow	0.01	Light Yellow
0.10	Light Orange	0.10	Yellow-orange
1.0	Light Orange	1.0	Orange
4.0	Bright Yellow	4.0	Red-brown
8.0	Pale Yellow		

Table 3: Observations of Color Following Decolorization Treatment of Acidified Urine with Amberlite XAD-7

[HNO ₃], M	Color of Liquid	Color of XAD-7 Beads	[MSA], M	Color of Liquid	Color of XAD-7 Beads
0.001	Nearly Colorless	Light Orange	0.001	Nearly Colorless	Light Orange
0.01	Nearly Colorless	Light Orange	0.01	Nearly Colorless	Light Orange
0.10	Nearly Colorless	Orange	0.10	Colorless	Orange
1.0	Nearly Colorless	Red-brown	1.0	Colorless	Red-brown
4.0	Light Yellow	Orange	4.0	Light Orange	Purple-brown
8.0	Pale Yellow	Pale Yellow			

Table 1 shows nearly quantitative recovery of strontium for charcoal at acid concentrations of 0.10 M and greater. All acid concentrations for XAD-7 treatment led to quantitative recovery of strontium. It is not certain why the recovery for XAD-7 and 0.001 M MSA is so high (114%). Prior work by Shkrob [personal communication, October 2009] suggests that MSA is more efficient at removing organic substances when combined with charcoal. Taking Sr-85 recovery with complete and rapid decolorization into account, we inferred that the suggested conditions for the pre-treatment of urine are acidification to 0.1-1.0 M MSA, contact with activated charcoal, and filtering before sending the stream to an extraction stage.

3. Metals Separations

In these studies, various extractant systems employing Diphonix® resin and Sr resin were evaluated for the rapid and efficient extraction of strontium from treated urine and urine simulants in the presence of alkali and alkaline earth elements.

For simplicity and ease of detection, all of the following experiments were performed with Sr-85, a radionuclide whose chief mode of decay is by electron capture to an Rb-85 isomer. The subsequent emission of a gamma ray (0.514 MeV) to ground-state Rb-85 is the detected event. All metal distribution coefficients (D_M) are calculated as weight distribution coefficients by

$$D_M = \frac{(C_0 - C_f)}{C_f} * \frac{V}{m},$$

where C_0 and C_f are the counts per minute for the control (pre-extraction) and sample (post extraction), respectively; V is the volume (in mL) of the liquid phase; and m is the mass (in grams) of resin or solid extraction phase.

All D_M dependency data are plotted in the accompanying figures with axes in logarithmic base 10 scale.

3.1 D_{Sr} versus [MSA] on Sr Resin

Since MSA is the leading reagent for urine pre-treatment, it was necessary to evaluate the effect of MSA on strontium extraction by Sr resin. If MSA could be used as a substitute for nitric acid on Sr resin, or if it did not interfere with extraction, then its use in pre-treatment would not require an extra step for its removal prior to a step using Sr resin. Demonstrating the effect of MSA on strontium extraction by Sr resin was achieved by contacting Sr-85 spiked aqueous MSA at various concentrations (0-4 M) with bulk Sr resin in the presence and absence of 3 M nitric acid. All samples were vortex mixed for

2 min, allowed to stand approximately 10 min, then vortex mixed for 10 sec frequently for the next 10 min and allowed to settle. To ensure that resin capacity was not exceeded and that subtle changes in strontium uptake could be observed, we used 1:50 and 1:20 (g/mL) ratios of wet resin to aqueous phase for samples with and without nitric acid, respectively. Due to a convergence in the densities of the resin and 3-4 M MSA solutions, we had to filter the suspended beads at these conditions. A general experimental scheme for the extraction and recovery determinations is given in Figure 1.

Figure 1: General Sample Preparation Procedure for Extraction and Recovery Determination

The summary of these results presented in Table 4 indicates that MSA has no effect on the uptake of strontium by Sr resin from 0 to 4 M in aqueous solution. In the presence of 3 M nitric acid, the D_{Sr} showed no dependency on MSA concentration. Even the minor reduction in D_{Sr} from 0 to 4 M MSA is within the actual experimental error estimated for these types of experiments ($\pm 10\%$). Moreover, in the absence of nitric acid, no significant extraction of strontium was possible.

Table 4: D_{Sr} vs. MSA Concentration on Sr Resin in Presence and Absence of Nitric Acid

Condition	D_{Sr}	Relative Uncertainty	Condition	D_{Sr}	Relative Uncertainty
3 M HNO ₃	150	0.9%	0 M MSA	1.95	1.5%
0.25 M MSA/3M HNO ₃	150	0.7%	0.25 M MSA	0.37	1.8%
0.50 M MSA/3M HNO ₃	157	1.9%	0.50 M MSA	0.23	0.7%
1.00 M MSA/3M HNO ₃	157	0.7%	1.00 M MSA	0.20	1.0%
1.50 M MSA/3M HNO ₃	160	2.3%	1.50 M MSA	0.33	0.2%
2.00 M MSA/3M HNO ₃	167	6.4%	2.00 M MSA	0.75	1.8%
3.00 M MSA/3M HNO ₃	164	5.7%	3.00 M MSA*	1.79	0.8%
4.00 M MSA/3M HNO ₃	138	1.6%	4.00 M MSA*	1.68	2.7%

* Samples filtered by Wheaton 25-PP disk filters to remove suspended resin beads

3.2 Why Diphonix® Resin for Initial Strontium Sorption?

Diphonix® resin is a geminally-substituted diposphonic acid gel-type resin with a strong affinity for trivalent and tetravalent metals. Constructed of a polystyrene/divinylbenzene matrix in a spherical bead form, this resin is polyfunctional, containing gem-diphosphonic and sulfonic acid groups bonded to the polymer matrix [8]. Figure 2 is a structural representation of the repeating functional groups in the polymer.

Figure 2: Structure of Diphonix Resin

Though Sr resin is demonstrably selective for strontium over most metals, it has neither the selectivity nor capacity to resolve strontium from the other metals present in urine at millimolar quantities. Previous methods have used a traditional pre-treatment of precipitation and ashing, followed by at least three columns with differing selectivities, in order to analyze multiple components in urine [9]. Running the pre-treated sample through Diphonix® resin before the Sr resin offers several advantages: selectivity, capacity, and compatibility with a low acid pre-treatment. As the first extraction chromatographic platform in the sample stream, Diphonix® resin can load all metals (to a reasonable concentration at a given resin-to-aqueous phase ratio) in a low acid matrix and elute strontium with a modest increase in acid. Adding concentrated nitric acid to the strontium elution volume to attain 3 M HNO₃ will then provide the conditions to load a Sr resin column. The Sr resin may be reserved for when other divalent metals need to be separated from strontium, especially calcium, for which it is well suited, having an Sr/Ca selectivity of 400 at 3 M nitric acid.

Iron, aluminum, actinides, and lanthanides are very strongly retained on the Diphonix® resin up to acidities as high as 4 M HNO₃ ($D \sim 10^2$ to 10^3 for trivalents and $D \sim 10^4$ for tetravalents) [10]. This relatively flat dependency is largely due to the formation of strong complexes with the phosphoryl groups by these metal species, without exchange of protons [10]. Consequently, the ubiquitous occurrence of Y-90 in secular equilibrium with Sr-90 is not likely to cause LSA interference, because Y(III) will be retained by the column under conditions that elute strontium. Acid dependencies for alkaline earth metals and alkali metals indicate metal uptake with the displacement of protons as an inverse function of acid concentration to the power of the charge on the ion. Thus, it is expected that D_{Sr} vs. $[H_3O^+]$ will have a slope of approximately minus two. Therefore, D_M for a given alkaline earth metal will often be an order of magnitude or greater than that of alkali metals under the same conditions.

Work by Dietz et al. summarizes the acid dependencies of alkaline earth metal uptake on Diphonix® resin and other ion-exchange resins [11]. Although alkaline earth retention is better on Bio-Rad AG 50W-X8 and AG MP-50 by orders of magnitude, these resins have cross-linked sulfonic acid functionalities only and are, therefore, not likely to behave like Diphonix® resin for trivalent and tetravalent metals. Our interest here is to analyze selectively and rapidly for radiostrontium only, and thus we have the luxury of batch separation and disposal of these other metals—alkali metals by washing, and trivalent and tetravalent metals by retention on the resin. It is important to note that for the Bio-Rad resins, strontium retention is quite strong over a wide range of acidities, complicating its subsequent recovery from the column.

Reasons for using Diphonix® resin in the initial cleanup of the urine matrix include the possibility of overloading a single extraction chromatographic column, the

requirement for a prohibitively large bed volume to achieve the desired separations on a column of Sr resin alone, and the need for extra steps to minimize interference from potassium and/or sodium. Millimolar quantities of sodium, potassium, and calcium found in human urine pose the greatest hurdle for retaining nanomolar to picomolar quantities of radiostrontium. Our efforts have, therefore, focused on gaining an understanding of the general retention characteristics of strontium on Diphonix resin and the competition between strontium, sodium, potassium, and calcium in a range of low MSA concentrations (0 to 0.4 M).

3.3 D_{Sr} versus MSA Concentration on Diphonix® Resin

The first step in characterizing Diphonix® resin with MSA, when all reported studies have involved nitric acid or hydrochloric acid, was to determine the MSA dependencies with and without nitric acid. Our approach was the same as the above Sr resin study, with the following differences: presence and absence of 0.5 M nitric acid and contact with Diphonix® resin (50-100 mesh) at 1:33 to 1:50 resin:aqueous ratios (g/mL). Strontium distribution data for different MSA acid concentrations in the presence and absence of 0.5 M nitric acid are given in Table 5. Figure 3 plots D_{Sr} versus the overall acid concentration for the MSA alone and MSA plus 0.5 M HNO_3 conditions. The curves reveal that for these two comparably strong acids ($pK_a = -1.5$ for HNO_3 and -2 for MSA), the retention of strontium is dominated by the cation-exchange mode, as described in the introduction to this section. No significant difference is observed in the curves for either set of conditions up to approximately 2 M acid. Assuming a 36% dry weight basis for the resin (based on triplicate results for 0.3 g of 100-200 mesh resin, data not presented), the curves in Figure 4 compare well with published nitric acid dependencies [12]. The chief differences between the published values and the “dry” D_{Sr} here may be due to the water content between the lot used for this study and that analyzed for water content. Therefore, it can be concluded that the use of MSA on Diphonix resin will result in the same retention of strontium as when using nitric acid.

Table 5: D_{Sr} vs. Acid Concentration with Diphonix® Resin
MSA + 0.5M HNO_3

[MSA]	[H_3O^+]	D_{Sr} (Wet)	D_{Sr} (Dry)	Notes
0	0.5	16.87	48.19	
0.25	0.75	8.00	22.85	
0.5	1	4.43	12.65	
1	1.5	2.07	5.91	
1.5	2	1.15	3.28	
2	2.5	-0.25	-0.71	not included on log-log plot
3	3.5	0.54	1.53	
4	4.5	0.73	2.09	
MSA only				
[MSA]	[H_3O^+]	D_{Sr} (Wet)	D_{Sr} (Dry)	Notes
0	0.15	160.86	459.59	This [H_3O^+] is not known. Assumption made based on tracer [HCl] = 0.0025M did not fit curve. Therefore, [H_3O^+] assumed based on slope = 2.
0.25	0.25	79.15	226.15	
0.5	0.5	15.79	45.11	
1	1	5.04	14.41	
1.5	1.5	2.30	6.56	
2	2	-1.95	-5.57	not included on log-log plot
3	3	0.87	2.49	
4	4	1.73	4.95

Figure 3: D_{Sr} vs. H_3O^+ Concentration on Diphonix® Resin (Wet Weight Basis)

Figure 4: D_{Sr} vs. H_3O^+ Concentration on Diphonix® Resin (Dry Weight Basis)

3.4 Strontium Uptake Suppression by Potassium and Calcium on Diphonix®

To assess the effect of potassium and calcium levels expected in normal human urine, we carried out an experiment to determine the concentrations of these metals that begin to suppress the extraction of strontium. Stock solutions were made from the salts $Ca(NO_3)_2 \cdot 4H_2O$ and KNO_3 at nominally 0.4 M salt in 0.40 M MSA. The calcium nitrate tetrahydrate salt stock was analyzed by ion chromatography with electrical conductivity detection to ensure an accurate concentration for Ca^{2+} . From the results of this analysis, the relative standard deviation (RSD) for triplicate measurements was 2.14%, with an average concentration of 0.338 M, and the standard calibrators deviated from 0.23% to

7.4% about the best-fit curve for the least-squares regression. From these stocks were prepared a series of dilutions in 0.40 M MSA for each salt, which were then spiked with Sr-85 tracer and contacted with Diphonix resin at a phase ratio between 1:50 and 1:40 (g/mL). The general procedure followed for the extraction is described in Figure 1.

The results of this experiment listed in Table 6, and plotted for D_{Sr} as a function of individual salt concentrations in Figure 5, show that suppression of strontium uptake on Diphonix® resin begins at approximately 0.005 M Ca^{2+} and 0.05 M K^{+} in 0.4 M MSA. Calcium is expected to diminish strontium retention more than alkali metals at a given concentration because of its second-order cation exchange modality. Given that calcium and potassium are present in normal human urine at 50 mM and 100 mM, respectively, and that these values can vary widely with diet and disease state, it would be reasonable to aim for at least a 10-50 fold reduction in one or both of these metals to avoid breakthrough of strontium upon washing a loaded Diphonix column.

Table 6: Sr-85 Uptake Suppression on Diphonix® Resin by Calcium and Potassium in 0.4 M MSA

$[Ca^{2+}]$, M	D_{Sr} (Wet)	D_{Sr} (Dry)	% Suppression
0	31	88	0
0.0004	28	81	8
0.0008	28	80	10
0.004	24	69	22
0.008	18	51	43
0.04	8.3	24	73
0.08	4.6	13	85
0.2	3.4	10	89

$[K^{+}]$, M	D_{Sr} (Wet)	D_{Sr} (Dry)	% Suppression
0	30	85	0
0.0005	31	88	-4
0.001	32	90	-6
0.005	30	87	-2
0.01	27	78	9
0.05	26	75	12
0.1	17	48	43
0.2	12	33	61

Figure 5: D_{Sr} vs. Ca^{2+} and K^+ Concentration in 0.40 M MSA on Diphonix® Resin for a Phase Ratio of 1:20 (g/mL, Wet Weight Basis) Measured by Radiotracer

These results have also been skewed by an over-loading of the resin. To evaluate this possibility, spot checks were performed at 0.1 M MSA and salt concentrations that correspond to approximately 50% suppression (or $D_w \sim 15$) under the above conditions (0.01 M Ca^{2+} and 0.1 M K^+ in 0.4 M MSA). The competition for the resin between metal species increased by approximately 30% when the H^+ concentration was reduced (see Table 7). These data indicate that nominal D_{Sr} values increased by two-fold by use of 0.1 M MSA from 0.4 M MSA. Achieving distribution ratios of 100 or greater at acid concentrations expected for loading of the species of interest is often a good sign for implementing the separation on a typical column size.

Table 7: Spot Checks for Sr Uptake on Diphonix® Resin Suppression by Ca^{2+} and K^+ in 0.1 M MSA

Metal	$[\text{M}^{n+}]$, M	D_{Sr}	Suppression, %
	0.00	436	
Calcium	0.01	108	75
Potassium	0.10	116	73

3.5 D_{Na} versus MSA Concentration on Diphonix® Resin

There is a dearth of published data for the uptake of alkali metals on Diphonix® resin. The simplest way to gather data on how sodium behaves on Diphonix® resin with respect to MSA concentration is to use a Na-22 tracer, which will give ideal behavior, although it will not reveal how sodium works at high millimolar quantities from urine. A series of aqueous MSA solutions was prepared and spiked with a Na-22 tracer. Samples were prepared and tested according to the diagram in Figure 1. Acid dependency data for both D_{Sr} and D_{Na} are displayed in Table 8 and plotted in Figure 6 for comparison. Note that the slopes for the linear portion of each curve (-1 for Na and -2 for Sr) indicate the displacement of hydrogen ions to the extent expected for ion exchange. Deviations from this behavior can be attributed to electrolyte intrusion and high ionic strength effects.

Table 8: D_{Na} and D_{Sr} vs. Acid Concentration on Diphonix® Resin

$[\text{H}_3\text{O}^+]$, M	$D_{\text{w, Na}}$	$D_{\text{w, Sr}}$	Notes
0.10	10		
0.15	--	161	This $[\text{H}_3\text{O}^+]$ is not known. Assumption made based on tracer $[\text{HCl}]$ from Sr-85 of 0.0025M, as D_{w} did not fit curve. Therefore, $[\text{H}_3\text{O}^+]$ assumed based on slope of 2.
0.25	4.1	79	
0.5	2.1	16	
1	--	5.0	Na Stock not acid-spiked with MSA.
1.5	0.69	2.3	
2	1.0	-2.0	$D_{\text{w, Sr}}$ not included on log-log plot.
3	6.0	0.87	
4	1.0	1.7	IX = ion exchange region of acid dependency
	Slope Na (IX)	Slope Sr (IX)	
	-1.1	-1.8

Figure 6: D_{Na} and D_{Sr} vs. H_3O^+ Concentration on Diphonix® Resin

3.6 D_{Sr} and D_{Na} versus MSA Concentrations with NaCl/KCl on Diphonix® Resin

A baseline for ideal behavior on Diphonix® resin was established by the previous work. Approaching the conditions expected for urine extractions, the addition of millimolar quantities of salts to the matrix was tested. In the interest of checking tracer data with macroscopic salt data in the same matrix, these acid dependencies were acquired by radiometric measurements and by inductively coupled plasma atomic emission spectrometry (ICP-AES). We explored the effect of varying MSA concentration at a phase ratio of 1:20 (g/mL) in the presence of 100 mM NaCl and 100 mM KCl on D_{Sr} and D_{Na} . Figure 7 shows acid dependency data for both D_{Sr} and D_{Na} determined with

radiotracers (see Figure 1), and Figure 8 shows comparable data obtained with ICP-AES.

Figure 7: D_{Na} and D_{Sr} vs. MSA Concentration with 100 mM NaCl/KCl on Diphonix® Resin for a Phase Ratio of 1:20 (g/mL, Wet Weight Basis) Measured by Radiotracer

Figure 8: D_{Na} and D_{Sr} vs. MSA Concentration with 100 mM NaCl/KCl on Diphonix® Resin for a Phase Ratio of 1:20 (g/mL, Wet Weight Basis) Measured by Radiotracer and ICP-AES (Na only)

Values for D_{Na} for each analysis method compare well with each other at 2%, 14%, and 16% difference between averages in 0.1 M, 0.2 M, and 0.4 M MSA, respectively. At 0.8 M MSA, these values begin to deviate from one another significantly. These data indicate that selectivity for Sr/Na drops by an estimated factor of three from acid-only solutions to 100 mM NaCl/KCl at a given low MSA concentration, for example, 0.2 M MSA. Therefore, a study was conducted to determine the effect on strontium and sodium extraction by Diphonix® resin by varying NaCl and KCl concentrations from 0 to 0.2 M each with 0.1 M and 0.2 M MSA. These experiments were performed for phase ratios of 1:10, 1:20, and 1:30 (g/mL) to simulate the washing

of a single-plate column with ten to thirty column volumes. These data would provide good input for the modeling of a column separation. Sample preparation was carried out by radiotracer analysis as described in Figure 1.

In Figure 9, the distribution ratios for strontium are plotted versus salt concentration and show very little differences across the three phase ratios, all other conditions being the same; the distribution ratios do not differ much and, in many cases, are almost identical. The largest difference occurs for the 0.1 M salt in 0.2 M MSA samples, where the RSD is 17%, which may be attributable to non-ideal behavior. All indications are that none of these phase ratios leads to an overloading of the resin. Figure 10 presents the D_{Sr} values versus ionic strength, which shows that, at least at ideal salt activities, the data are reproducible. Verification of the distribution ratio for strontium (converted to wet weight basis based upon results in Section 3.3) for 0.1 M salt in 0.1 M MSA at the 1:20 phase ratio is 6% different from the replicate condition found in Figure 8. Additionally, when the MSA concentration is increased two-fold, the distribution ratios diminish by roughly four-fold, which follows the inverse second-order function expected for Sr^{2+} ion exchange.

Figure 9. D_{Sr} vs. NaCl/KCl Concentration in 0.1 M and 0.2 M MSA on Diphonix® Resin (Dry Weight Basis) for 1:10, 1:20, and 1:30 Phase Ratios (g/mL)

Figure 10: D_{Sr} vs. Ionic Strength (I) in 0.1 M and 0.2 M MSA on Diphonix® Resin (Dry Weight Basis) for 1:10, 1:20, and 1:30 Phase Ratios (g/mL)

We acquired data for sodium uptake by Diphonix® resin using a Na-22 tracer and the same experimental design indicated in Figure 1. Examining the data in Figures 11 and 12 will again show that the capacity of the resin is not exceeded in even the highest phase ratio (1:30) based on the convergence of all these values under the same conditions. Summarized data from the Sr and Na experiments are shown in Table 9, where the selectivity factor for strontium over sodium is listed in the last column. Selectivity factors are between 8 and 37 for 0-0.2 M salt in 0.1 M MSA and 6 and 19 for 0-0.2 M salt in 0.2 M MSA. These values are good, considering that, for columns with reasonable plate numbers, selectivity factors of 2 to 3 can separate two metals.

Figure 11: D_{Na} vs. NaCl/KCl Concentration in 0.1 M and 0.2 M MSA on Diphonix® Resin (Dry Weight Basis) for 1:10, 1:20, and 1:30 Phase Ratios (g/mL)

Figure 12: D_{Na} vs. Ionic Strength (I) in 0.1 M and 0.2 M MSA on Diphonix® Resin (Dry Weight Basis) for 1:10, 1:20, and 1:30 Phase Ratios (g/mL)

Table 9: Acid Dependency Data for Sr and Na Extraction by Diphonix® Resin from 0-0.2 M NaCl/KCl in 0.1 M and 0.2 M MSA for 1:10, 1:20, and 1:30 Phase Ratios (g/mL)

0.1 M MSA					
[NaCl]/[KCl], M	Ionic Strength (ideal)	Resin:Liquid (w/w)	D _{Sr} (dry)	D _{Na} (dry)	Selectivity (D _{Sr} /D _{Na})
0	0.1	1:10	700	20.5	34
0.01	0.12	1:10	480	17.1	28
0.05	0.2	1:10	173	10.3	17
0.1	0.3	1:10	80	7.46	11
0.2	0.5	1:10	33	4.79	7
0	0.1	1:20	791	21.3	37
0.01	0.12	1:20	495	17.0	29
0.05	0.2	1:20	179	10.8	17
0.1	0.3	1:20	82	6.52	13
0.2	0.5	1:20	36	4.49	8
0	0.1	1:30	762	22.2	34
0.01	0.12	1:30	532	18.4	29
0.05	0.2	1:30	180	10.0	18
0.1	0.3	1:30	84	7.22	12
0.2	0.5	1:30	36	4.50	8
0.2 M MSA					
[NaCl]/[KCl], M	Ionic Strength (ideal)	Resin:Liquid (w/w)	D _{Sr} (dry)	D _{Na} (dry)	Selectivity (D _{Sr} /D _{Na})
0	0.2	1:10	191	11.0	17
0.01	0.22	1:10	159	9.22	17
0.05	0.3	1:10	83	7.22	11
0.1	0.4	1:10	39	5.66	7
0.2	0.6	1:10	20	3.61	6
0	0.2	1:20	202	11.2	18
0.01	0.22	1:20	166	9.70	17
0.05	0.3	1:20	86	6.77	13
0.1	0.4	1:20	47	5.24	9
0.2	0.6	1:20	24	3.28	7
0	0.2	1:30	207	11.4	18
0.01	0.22	1:30	177	9.29	19
0.05	0.3	1:30	91	6.75	14
0.1	0.4	1:30	55	4.36	13
0.2	0.6	1:30	25	2.07	12

3.7 D_{Sr} versus MSA Concentration in Urine on Diphonix® Resin – Urine Treated with MSA and Charcoal

Characterization of strontium extraction on Diphonix® resin had started with ideal acid dependencies and reached the point of roughly simulating the ionic strength of urine. We next estimated D_{Sr} for an actual urine sample. In addition to these sodium and potassium salts, urine contains about 0.2-0.6 M urea, 20 mM phosphates, creatinine, and urate. Initially, we did not know whether or not these organic components interfere with Diphonix® resin extraction. The concern was that D_{Sr} for urine can turn out to be significantly lower than that in the salt mixture.

Three milliliter aliquots of uncertified urine were acidified with neat MSA to give concentrations of 0, 0.1, 0.2, 0.3, and 0.4 M MSA, nominally. A Sr-85 tracer was added in quantity sufficient to attain rates of approximately 5000 counts per minute for the control samples. At a ratio of 1:100 (g/mL), the acidified and spiked urine was added to glass vials with activated charcoal. The procedure followed is shown in Figure 1. This procedure was also followed for Diphonix® resin extraction at 1:10, 1:20, and 1:30 phase ratios (g/mL, wet). Triplicate samples were taken for all controls and samples. The data are given in Tables 10 and 11 and Figure 13.

Table 10: Strontium Recoveries from Acidified Urine Charcoal Treatment

[MSA], M	Charcoal Recoveries (n=4)	Relative Uncertainty
0	34.9%	5.2%
0.1	98.4%	3.8%
0.2	97.4%	3.5%
0.3	101%	3.1%
0.4	99.7%	3.2%

Table 11: Average Acid Dependencies for Strontium Extraction from Acidified, Charcoal-Treated Human Urine

Diphonix 1:10 (w/V)			
[MSA], M	D_{Sr} (wet)	D_{Sr} (dry)	RSD
0	1228	3427	3.3%
0.1	112	313	2.0%
0.2	38.3	107	1.5%
0.3	16.5	45.0	0.3%
0.4	12.5	36.3	0.5%
Diphonix 1:20 (w/V)			
[MSA], M	D_{Sr} (wet)	D_{Sr} (dry)	RSD
0	1565	4366	5.7%
0.1	108	301	0.7%
0.2	38.7	108	0.8%
0.3	19.6	54.7	0.5%
0.4	12.4	34.7	0.3%
Diphonix 1:30 (w/V)			
[MSA], M	D_{Sr} (wet)	D_{Sr} (dry)	RSD
0	1776	4956	6.7%
0.1	102	285	1.4%
0.2	38.5	107	1.2%
0.3	19.6	54.6	0.7%
0.4	12.4	34.6	0.6%

Figure 13: D_{Sr} vs. MSA Concentration in Human Urine on Diphonix® Resin for 1:10, 1:20, and 1:30 Phase Ratios (g/mL, wet)

All samples containing acid showed no significant losses of strontium to the charcoal treatment, as expected from what Sadi et al. [7] had found. Average D_{Sr} values for all of the ratios are extremely reproducible, between 0.3% and 2.0% RSD, when MSA is present (Table 11). This is evidence of loading under resin capacity for all ratios. As predicted from the salt simulations, our data in the plot (Figure 13) show that the phase ratios do not affect the distribution of strontium, thus confirming that capacity is not likely to be an issue with normal human urine. When compared to the D_{Sr} data for the salts at 0.1 M and 0.2 M MSA, the treated urine behaved like 0.075 M and 0.1 M salts at these MSA concentrations, respectively. Perhaps, if the urine used is comparable in make-up to normal human urine, then this separation is practical, and the next stage (Sr resin) should be added to the next set of experiments.

4. Conclusions

To summarize, we have demonstrated that urine can be efficiently decolorized and freed of organics by treatment with either nitric acid or MSA followed by contact

with activated charcoal or an appropriate polymeric sorbent. In addition, we have shown that the removal of organics is not accompanied by measurable loss of radiostrontium from the sample. Sorption of strontium by a commercial, diphosphonic acid-based ion-exchange resin (Diphonix) from acidic aqueous phases containing MSA follows the trend expected for simple ion exchange. This sorption is diminished by high levels of common cationic constituents of urine, in particular, K^+ , Na^+ , and Ca^{2+} , but the adverse effect of these ions is not sufficient to preclude the use of Diphonix as a first step in the separation and preconcentration of Sr-90 from urine for subsequent determination by liquid scintillation analysis.

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