The Use of Ion Exchange for the Determination of Radioelements in Large Volumes of Urine[1]

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The efficacy of ion exchange as a means of extracting, concentrating, and purifying cations and anions from large volumes of solutions is well known. Inasmuch as the determination of radioelements or trace elements in urine involves similar problems it was felt that analogous adsorption procedures could be applied. Numerous studies had already demonstrated the ability of ion exchangers to extract ions, particularly calcium, from biological fluids (*1*). Our objective was to extract quantitatively a trace element from a liter or more of urine and concentrate it in a few ml of a solution completely free from the large concentration of salts which usually interferes with spectrographic and chemical methods of analysis.

In connection with various metabolic studies it was desirable to determine quantitatively the concentrations of fission products in urine, especially with regard to relating the urinary levels of radioelements to body content. Since the rare earths constitute an important fraction of the fission products, the determination of these elements in urine by using a cation exchanger was attempted. Carrier-free radioyttrium, Y^{91}, was chosen as a tracer element for these studies. An extensive investigation of optimum conditions was made, but only the most recent workable flow sheet is presented.

The principles involved in the adsorption and desorption of a cation from an organic cation exchanger are discussed elsewhere (*2*, *3*). Essentially the cation exchange reactions follow the law of mass action. A given reaction, then, can be made to proceed in any direction by altering the relative concentration of the reactants and products. In this adsorption process for extracting and subsequently eluting yttrium from urine, the principal reaction for both the adsorption and desorption steps is:

$$Y^{+++} + 3HR \underset{\text{Desorption}}{\overset{\text{Adsorption}}{\rightleftharpoons}} YR_3 + 3H^+,$$

in which the symbol *R* represents the nondiffusible anionic part of the cation exchanger.

The adsorption of the yttrium is made from urine, 0.1 M in HCl, while the desorption is carried out with 7 M HCl. Briefly, the adsorption process consists of passing a liter of acidified urine containing tracer yttrium through an adsorption column of a cation exchange resin, removing the extraneous calcium and other cations with 0.4 M HCl, and subsequently eluting the adsorbed Y^{+3} with a small volume of 7 M HCl. The 7 M HCl is evaporated to near dryness to remove the bulk of the acid, while remaining organic matter is destroyed by wet ashing with nitric acid. The residue is transferred quantitatively with distilled water to a 10-ml capacity porcelain capsule, evaporated to dryness under an infrared bulb, and the radioactivity is measured directly with an end mica-window Geiger-Müller counter.

If the radiations from a particular radioelement are not very penetrating, it is necessary that the last traces of salts be removed. With Y^{+3}, for example, it is possible to dilute the ashed residue with distilled water and pass it through a second column of adsorbent which contains only $\frac{1}{17}$ by weight as much resin as is present in the first column. The adsorbed Y^{+3} is eluted with 60 ml of 7 M HCl. When evaporated to dryness, mounted on a flat platinum plate, and flamed, this solution leaves, in most cases, no perceptible residue.

The advantages claimed for the method are: (1) no preparation of the urine other than acidification is necessary; (2) no close control of pH is required; (3) the operation may be interrupted at any stage desired; (4) one technician can run several samples simultaneously; and (5) the equipment and adsorbent, once set up, may be used repeatedly.

Amberlite IR-1 resin[4] is employed in the first column adsorption step while a more insoluble resin, Amberlite IR-100H, is used in the second step because it helps to minimize the amount of solid matter associated with the yttrium. The weights of resin are expressed in terms of the air-dried hydrogen form. Now that more insoluble and higher capacity resins, such as Dowex 50[5] (*2*) and Amberlite IR-120, are available it would be definitely advantageous to substitute them for IR-1 and IR-100H after making allowances for the capacity and kinetic characteristics of these new resins (*2*, *4*).

The glass columns are set up in the usual manner. Glass wool serves as a satisfactory support for the resin bed. A straight glass stopcock is used to regulate the flow rates. A 2-l leveling bottle serves as a storage tank for liquids percolating through Column I while a 500-ml leveling bottle suffices for Column II. About 2′ of head is found to provide satisfactory flow rates. The urine was "spiked" with carrier-free Y^{91} and then acidified as specified in the flow sheet.

The accompanying flow sheet (Fig. 1) provides all the details of the operations necessary for the extraction and concentration of Y^{91} from liter volumes of urine. Larger volumes of urine can be handled by a proportionate increase in the mass of resin employed. The resin is ready for a new run at the end of each cycle.

The functions of the different solutions employed are as follows:

(1) The acidification of the urine prevents the precipitation of calcium salts, keeps the yttrium in ionic form,

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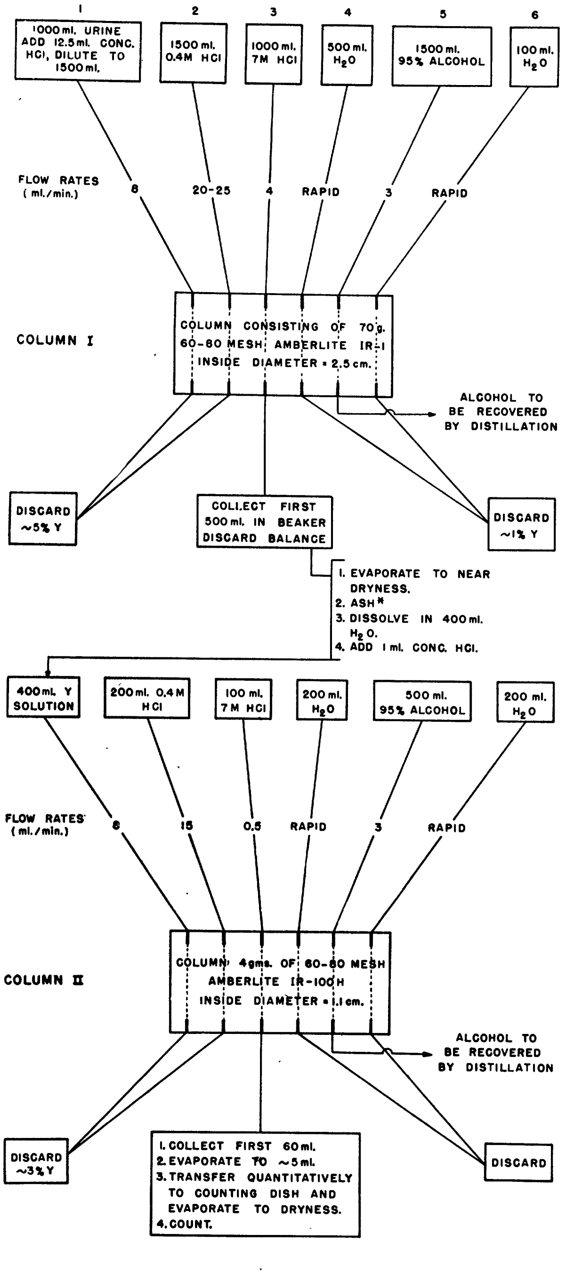

*THE SOLUTION, CONTAINED IN A 1 LITER BEAKER, IS EVAPORATED ON A HOT PLATE TO NEAR DRYNESS. THE ORGANIC RESIDUE IS DESTROYED BY THE ADDITION OF ABOUT 20 ml. OF 1:1 HNO_3 AND EVAPORATED TO DRYNESS. THIS TREATMENT IS REPEATED AT LEAST TWO MORE TIMES. FINALLY TO THE ASHED MATERIAL IS ADDED 10 ml. OF 1:1 HNO_3 AND THE MIXTURE IS EVAPORATED TO NEAR DRYNESS.

FIG. 1. Flow sheet for the determination of radioyttrium, Y^{91}, in human urine by cation exchange.

and breaks up any unadsorbable complexes that yttrium may form with urinary constituents.

(2) The 0.4 N HCl removes some adsorbed organic matter as well as calcium and other monovalent and divalent cations.

(3) The 7M HCl serves to elute the yttrium quantitatively in a small volume.

(4) The 95% alcohol removes remaining organic matter. This step was introduced when it was found that the adsorption of yttrium from liter quantities of urine kept decreasing, *i.e.*, the break-through point was quite erratic and as much as 35% of the yttrium lost. It was presupposed that alcohol-soluble organic matter coated the resin particles so that the adsorption of yttrium was hindered. The alcohol wash was found to prevent the premature break-through of yttrium.

The adsorption method as it now stands gives consistent recoveries of Y^{91} of $90 \pm 5\%$ when only Column I is utilized, and an over-all recovery of $85 \pm 5\%$ if the process includes Column II. It is possible to improve this recovery by closer control of variables. The effect of yttrium concentration on its adsorption by the resin may be calculated (*4*). In the present process it appears that about 10^{-4} M of yttrium can be extracted with no loss in efficiency.

Because the concentrations of substances such as albumin and urea which normally appear in urine are quite variable, it was desirable to ascertain their effects on yttrium adsorption.

Albumin: The presence of albumin in urine as high as 2 gm/l had no observable effect.

Urea: In the range of concentration studied, 0–4.0 gm of urea/100 ml of urine had no effect on yttrium adsorption.

Acids: The equilibrium adsorption of yttrium by IR-1 from urine acidified with each of the following acids was studied: acetic, sulfuric, hydrochloric, and nitric in concentrations ranging from 0.1 N to 1.0 N. The maximum adsorption (which was about the same for the various acids) was obtained when the solutions were 0.1–0.2 N. Higher concentrations of acids caused a marked decrease in yttrium adsorption.

Sodium chloride: Concentrations of NaCl up to 1.2% did not reduce the adsorption of yttrium.

In general, the scheme given here will be found suitable for the extraction and concentration of other cations with a valence of +3 or greater. The processing of divalent cations such as Ba^{++} and Ra^{++} would involve a closer attention to the concentration and volume of the HCl-eluting solution in order to remove selectively urinary calcium. Chromatographic complex elution with citrate solutions can, of course, be utilized for the separation of calcium from other divalent cations (*4*). For metals which easily form complex anions, such as chromium, gold, and molybdenum, for example, an anion exchange system (*5*) may be found useful.

References

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