March 10, 1959 E. R. TOMPKINS ET AL 2,877,093

ADSORPTION METHOD FOR SEPARATING METAL CATIONS

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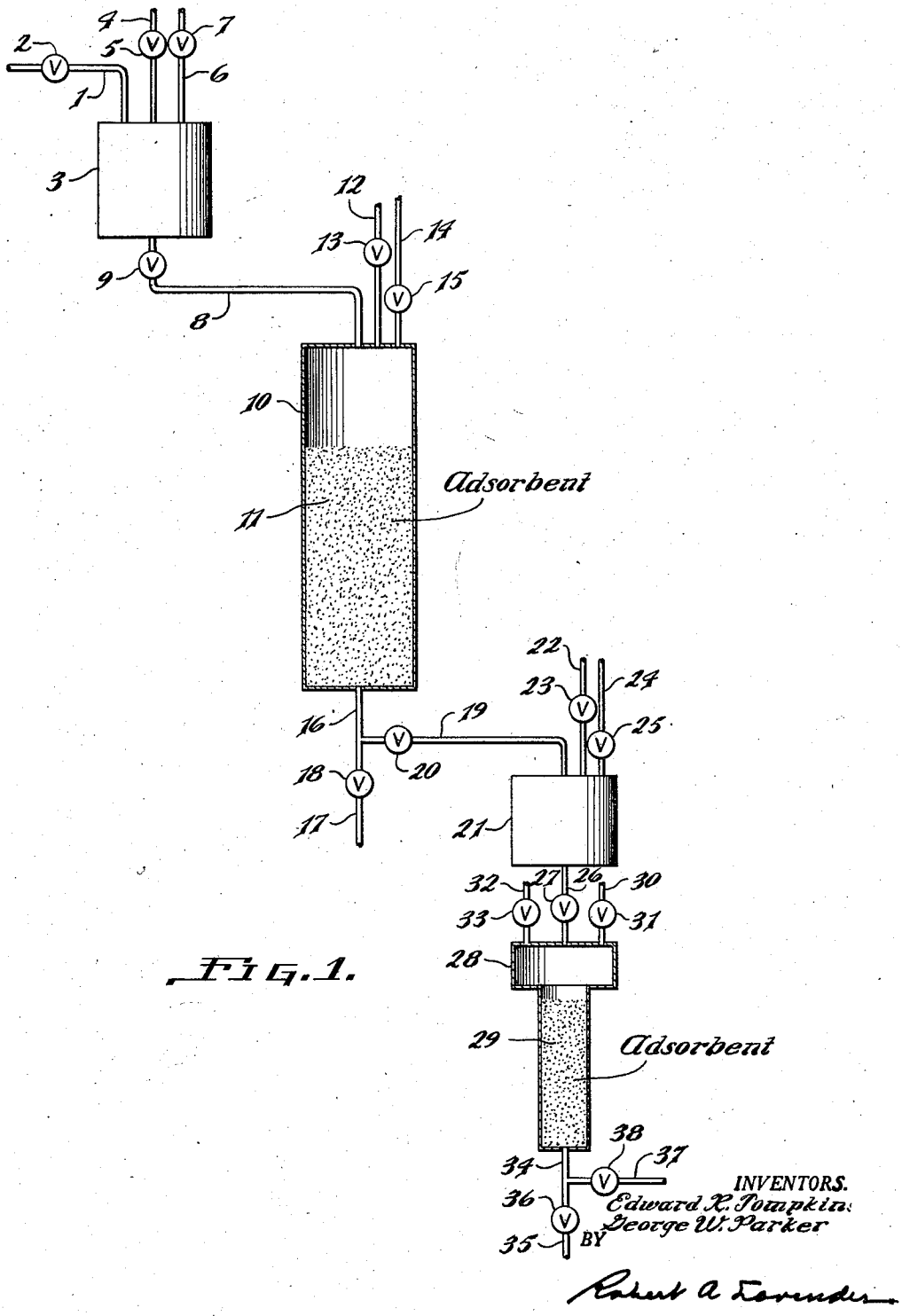


Fig. 1.

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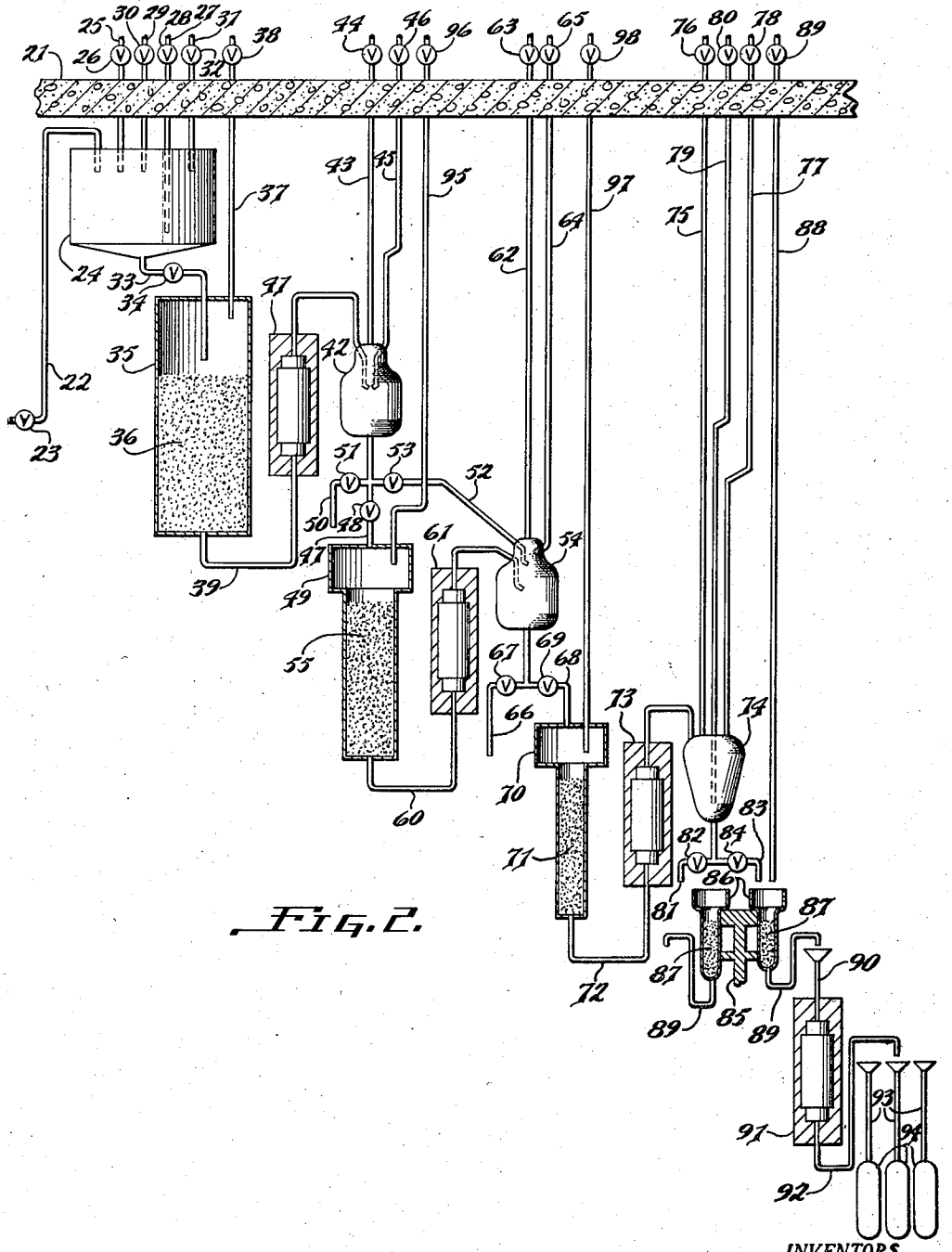


Fig. 2.

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2,877,093

ADSORPTION METHOD FOR SEPARATING METAL CATIONS

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Application April 25, 1946, Serial No. 664,958

12 Claims. (Cl. 23—23)

This invention relates to the separation of substances by means of chromatographic adsorption, and more particularly to a method of separating cations contained in a solution which involves adsorbing the cations upon an adsorbent and eluting the desired cations from the adsorbent in which method a substantial reduction in volume is obtained.

In many technical processes, it is often desirable to separate the components of various solutions either in the form of groups of these components or as individual components. For example, an extremely important field wherein such a separation process is utilized is that involving the separation of the components of a neutron irradiated uranium mass. The separation of the components of a neutron irradiated mass is extremely complicated, not only due to the extremely small quantities of the individual components present, but also to the high radioactivity of the material under treatment.

As described herein, the isotope of element 94, having a mass of 239, is referred to as 94^{239} and is also called plutonium, symbol Pu. In addition, the isotope of element 93 having a mass of 239 is referred to as 93^{239} and is called neptunium, symbol Np. Furthermore, the term "values" or its equivalent when employed herein with reference to an element is intended to embrace the element and compounds thereof. For example, the term "plutonium values" is intended to include plutonium as well as compounds thereof. The term "activity" or its equivalent when employed herein with reference to a radioactive element is intended to include the radioactive element and compounds thereof. For example, the term "barium activity" as employed herein is intended to include radioactive barium as well as compounds thereof.

Naturally occurring uranium contains a major portion of $_{92}U^{238}$, a minor portion of $_{92}U^{235}$ and small amounts of other substances such as UX_1 and UX_2. When a mass of such uranium is subjected to neutron irradiation, particularly with neutrons of resonance or thermal energies, $_{92}U^{238}$ by capture of a neutron becomes $_{92}U^{239}$ which has a half life of about twenty-three minutes and by beta decay becomes 93^{239}. The 93^{239} has a half life of about 2.3 days and by beta decay becomes 94^{239}. Thus, neutron irradiated uranium contains both 93^{239} and 94^{239}, but by storing irradiated uranium for a suitable period of time, the 93^{239} is converted almost entirely to 94^{239}.

In addition to the above mentioned reaction, the reaction of neutrons with fissionable nuclei such as the nucleus of $_{92}U^{235}$ results in the production of a large number of radioactive fission products. For example, when an atom of $_{92}U^{235}$ undergoes fission, two fragments are formed. These fragments vary sufficiently in their masses and hence their atomic numbers to give some 34

elements, all of which initiate further reaction chains with the emission of radiations. These chains are the source of all of the radioactivity that renders isolation of any one of the products of irradiation of uranium so difficult. The radiations include: (1) beta or high speed negative electrons with variable energy contents, and therefore, different velocities, (2) soft gamma, or electro-magnetic radiation similar to X-rays but with a shorter wave length and moderately higher energy content, (3) hard gamma similar to the soft type except that it has a shorter wave length and higher energy content, and (4) neutrons.

In general, the stability of an atom depends on the ratio of protons to neutrons in the nucleus and certain ratios, therefore, result in an excess energy content that must be emitted as radiation before a stable end product is formed. While most naturally occurring isotopes are stable and therefore not radioactive, those resulting from fission have proton-neutron ratios such as to cause internal instability. As a result, they tend to stabilize and in the process emit their excess energies in one of five general ways.

In the first place, an atom may emit a beta particle from the nucleus where the only possible source of a negative electron is from a neutron which gives both a positive and negative charge. The loss of the negative charge converts the neutron to a proton and there is a gain of one in atomic number and hence a transmutation to the next higher element. Such a change, of course, alters the proton to neutron ratio and may result in a stable atom, although this is not necessarily true.

In the second place, a beta particle of lower energy content may be emitted, thus forming the next higher element while still leaving the nucleus with too great an energy content to be stable. The first beta particle may then be followed by another one to form the second higher element in the atomic series which again may or may not be stable.

Thirdly, a beta particle of intermediate energy may be emitted to form an unstable isotope of the next higher element which, due to its excess energy, may give off a gamma ray rather than a beta particle. This process also may result in either a stable or an unstable atom.

Fourthly, the beta-decay of a fission product may leave the nucleus in a state of excitation higher than the binding energy of a neutron in that nucleus. The neutron is then immediately emitted, and the rate of decay of the neutron-emitting activity observed is just that of the preceding beta activity.

Finally, an unstable atom may emit a gamma ray which strikes an electron in one of the inner shells of electrons and ejects it in such a condition that it has some of the properties of the nuclear beta particle. Since the electron, which in this case is known as photoelectron, does not originate in the nucleus, there is no change in the atomic number and the process, like that involved in the emission of a gamma ray, is known as internal conversion.

With the exception of elements 43 and 61, the fission products formed by the above discussed reaction are all well known elements with normal chemical properties, the only point of difference between them and the natural element being that they are composed of unstable isotopes. As brought out above, due to their internal instability they either undergo transmutation to other elements or stabilize themselves internally by the emis-

sion of one or more of the previously-mentioned radiations. Consequently, stabilization may involve no change in atomic number or a change of several units. The average length of the fission chains, that is the number of transmutations, is about 3.2 but some may be as long as 6. In general, a chain reaction has emitted a total of 25 to 30 m. e. v. as radiation by the time it is complete.

The fission of $_{92}U^{235}$ yields two general types of elements, namely heavy and light. The light fission products possess atomic numbers between 30 and 46 and include radioactive zinc, gallium, germanium, arsenic, selenium, bromine, krypton, rubidium, strontium, yttrium, zirconium, columbium, molybdenum, 43, ruthenium, rhodium, and palladium.

The heavy fission products resulting from neutron irradiation of $_{92}U^{235}$ possess atomic numbers ranging from 47 to 63 and include radioactive silver, cadmium, indium, tin, antimony, tellurium, iodine, xenon, cesium, barium, lanthanum, cerium, praseodymium, neodymium, 61, samarium and europium.

Generally speaking, the irradiation of uranium is conducted under such conditions as result in the combined amount of neptunium and plutonium being equal to approximately 0.02% by weight of the uranium mass. The concentration of the fission products in neutron irradiated uranium is approximately the same as that of the total of the plutonium and neptunium. However, since many of the fission products are radioactive, they change to other elements at certain fixed rates which are characteristic of each fission product. In other words, they have fixed decay rates. Plutonium, on the other hand, is relatively stable, and since the fission products have varying decay rates, the concentration of the initially formed radioactive fission products with respect to plutonium changes substantially during the course of the reaction and particularly during the storage period which is generally employed after the neutron irradiated uranium has been removed from the reaction zone.

The quantities of the various individual radioactive fission products present in neutron irradiated uranium are extremely small and are generally referred to in the art as "tracer quantities."

As used herein, the terms "tracer" and "tracer quantity" or their equivalents are employed as definitive of extremely small amounts of radioactive materials. For example, radioactive materials in concentrations of 10^{-10} to 10^{-14} molar are considered to be tracer quantities. Such extremely small amounts are incapable of identification by ordinary micro analytical methods, and are, therefore, generally identified by the radiations emitted therefrom by means of any of the usual counting mechanisms known to the art.

As illustrative of a typical neutron irradiated mass containing fission products the following tables are given:

TABLE A

Distribution of beta activity in neutron irradiated uranium for each fission element as percentage of total

Element	Cooling Time		
	30 Days	60 Days	100 Days
Ce	15	20	27
Sr	18	24	26
Y	17	22	23
Zr	6.8	9.6	12
Ru	2.6	3.4	3.5
Cb	1.3	2.2	3.4
Pr	8.0	3.9	0.72
Cs	0.15	0.33	0.72
La	13	5.5	0.72
Te	0.87	0.86	0.67
Ba	9.5	4.0	0.52

TABLE B

Distribution of effective gamma activity in neutron irradiated uranium for each fission element as percentage of total

Element	Cooling Time		
	30 Days	60 Days	100 Days
Cb	14	30	40
Zr	18	25	26
Ce	4.4	6.6	10
Ru	7.5	9.0	8.6
Sr	6.3	6.9	4.8
La	38	16	2.3
Y	1.8	2.4	2.3
Te	.85	0.70	0.79
Cs	.15	0.30	0.55
Ba	4.1	1.8	0.24
Pr	1.9	0.4	----------
I	1.1	0.15	----------

As illustrative of the method of obtaining the data for the above tables, the following is given. A mixed fission product solution is subjected to counting and is found to have a total beta activity of 453,600 counts/minute/milliliter. To a 1.00 ml. sample is added 20.0 mg. of Ru and by appropriate chemical manipulation the Ru is isolated and purified. The final precipitate of metallic Ru weighs 18.0 mg. and gives 4950 counts/minute. The chemical yield is therefore 90% and the count, corrected for chemical yield, is 5500 counts/minute or 1.21% of the total activity.

From the above tables it can be seen that certain fission products are listed as both beta emitters and gamma emitters. This situation results from the presence in neutron irradiated uranium of various isotopes of the elements which comprise the fission products. Thus, one isotope of an element may be a beta emitter while another isotope may be a gamma emitter. Furthermore, and as is more generally the case, certain of the isotopes may emit both types of radiation.

Some members of both the light and heavy groups of fission products may be readily separated from the neutron irradiated uranium mass in that they have been found to have chemical properties similar to the rare earths and can, therefore, be isolated by precipitation under carefully controlled conditions with about one hundred times their weight of carriers such as lanthanum fluoride, bismuth phosphate, and the like. However, many of the fission products in both groups do not respond to such treatment and considerable difficulty has been experienced not only in attempting to separate plutonium values from these fission products, but also in attempting to isolate certain of the fission product values in carrier-free radioactive form.

It can be seen from the above discussion that the separation and isolation of the various products formed as a result of the neutron irradiation of uranium is an extremely difficult task, particularly in view of the fact that extremely small quantities of the individual fission products are present in the materials under treatment. The problem is further complicated by the presence of the various isotopes and the fact that the elements, considered to be formed at the time of fission, may actually represent conversion products from certain of the fission products which have undergone extremely rapid change; that is, those fission products having extremely short half lives. In this connection, approximately 155 isotopes of the fission products involved have been identified and about 30% of these have half lives of over eight hours. Fission products have been identified that have half lives ranging from about 3 seconds to 10^4 years.

Since, as pointed out above, the fission product values contained in a solution of neutron irradiated uranium even after a considerable period of storage exhibit radioactive properties, it is particularly advantageous not

only to separate these fission product values from plutonium values, but it is also advantageous in certain instances to isolate certain of the fission product values in carrier-free radioactive form in that they serve as an excellent source of radioactivity which may be utilized, among other things, in various fields such as medicine and metallurgy.

Among the methods which have been utilized in the separation of the components of a neutron irradiated uranium mass is that which is generally known as chromatographic adsorption. In the chromatographic adsorption process, a solution of neutron irradiated uranium is passed over a body of adsorbent of such character as to adsorb from the solution the desired components which are generally in the form of cations. Following the adsorption of cations, the adsorbent is then subjected to a treatment with a suitable material which may selectively remove the desired component from the adsorbent or which may selectively remove a group of desired components from the adsorbent. This removal step is generally termed elution, and is generally carried out by washing the body of adsorbent with a liquid adapted to remove the desired material under controlled conditions.

Such chromatographic adsorption for the separation of substances present in a solution of neutron irradiated uranium may be carried out with a wide variety of adsorbents including both inorganic adsorbents—such as silica gel, diatomaceous earth, or the like—and organic adsorbents—such as activated carbon, sulphonated carbonaceous material (zeo-carb), phenol-formaldehyde resins preferably containing free sulphonic acid groups, and the like. Particularly advantageous results are obtained in the first portion of the process by the use of ion exchange adsorbents, in which the cation of the adsorbent is exchanged for a similarly charged ion of the substance to be adsorbed. It has been found that the process is particularly effective where the adsorbent used is a relatively inert organic material containing free sulphonic acid groups. Thus, the adsorbent may comprise phenol-formaldehyde resins, lignite, phenol-tannic acid resins, or the like, which contain numerous R—SO_3—R′ groups, in which R is an organic group such as a methylene group and in which R′ is hydrogen or a metal ion, although R′ is preferably H^+ or Na^+. A particularly satisfactory adsorbent which may be employed is a phenol-formaldehyde condensation product containing methylene sulphonic acid groups (—CH_2SO_3H). In the adsorption process, the hydrogen of the sulphonic acid group is replaced by a cation of the substance to be adsorbed which thereupon forms a more or less loosely associated molecule with the residue.

The adsorbed material may then be separated from the adsorbent in any of a number of ways depending upon the desired material. For example, it has been found that uranyl nitrate solution may be separated nearly quantitatively into three fractions by means of chromatographic adsorption resulting in a fraction rich in U, a fraction rich in Pu and a fraction rich in mixed fission products. The fractionation may be accomplished when utilizing a resin of the type described above by the specific elution from the resin of UO_2^{++} with $SO_4^=$ and of Pu with $NaHSO_4$, the adsorbed fission products being then disposed of en masse with strong acid or sodium salt solutions.

It is also possible to remove specific components of a neutron irradiated uranium mass by controlling the conditions of adsorption and elution. For instance, the specific elution of individual fission products may be accomplished by organic acid-salt mixtures at controlled pH's.

Generally speaking, there are two methods of eluting adsorbed cations from a resin adsorbent of the type described above, both of which require the physical replacement of the adsorbed cation by another.

One method involves the addition of a cation possessing a greater resin affinity either intrinsically or by virtue of concentration. For example Ba^{++} replaces Sr^{++} of equivalent concentration by virtue of its greater affinity for the anion of the ion-exchange resin whereas Sr^{++} replaces Ba^{++} only if its concentration is somewhat greater than that of the Ba^{++}.

Another method involves lowering the effective concentration of the particular cation by complex formation, permitting its replacement by ions which ordinarily do not replace it. For example, Zr replaces H^+, but H^+ will replace Zr if oxalate is present to form the negatively charged zirconium oxalate complex which has no affinity for ion exchange resins of the type herein described.

The last mentioned type of elution is a particularly advantageous method of recovering individual fission products from an ion exchange resin type of adsorbent.

As an example of a method by which a sulphonated resin may be prepared, 175 parts of 1-hydroxybenzene-4-sulphonic acid are heated together with 40 parts of a formaldehyde solution of 30% strength for one-half hour to about 105° C. Then, further 60 parts of formaldehyde are added and the temperature is kept for about ten hours at 90° C. A hard black resin is formed which is stable to water and of conchoidal fracture. This resin is washed with water and ground to a powder. By regeneration with an acid or a solution of common salt, this base-exchanging body regains its original adsorption capacity.

While excellent separation has been obtained by use of the chromatographic adsorption process as outlined above, a considerable problem is presented by reason of the tremendous volumes of solution required to effect separation. This is particularly so in connection with the use of chromatographic adsorption for the separation of substances from solutions of neutron irradiated uranium in that the substances most desirable to separate, plutonium and the individual fission products, occur in very small quantities compared to the volume of liquid necessary to dissolve the uranium.

In addition, the use of chromatographic adsorption as a step in an overall separation process is handicapped as far as its use in connection with the separation of components of a neutron irradiated mass is concerned in that it is generally the practice to separate plutonium by precipitation methods and the resulting solutions containing fission products are even more diluted by reason of the added reagent solution.

It is accordingly an object of this invention to provide a simple and efficient method of reducing the volume of liquid to be handled in chromatographic absorption separation methods.

A further object of this invention is the provision of a method of separating the components of a solution by adsorbing on an adsorbent, eluting the desired components to obtain a more concentrated solution thereof, and passing the resulting concentrated solution through at least one smaller body of adsorbent and eluting to obtain further concentration.

Still another object of this invention is the provision of a system including a plurality of successively smaller adsorption zones to effect the concentration and/or separation of radioactive substances contained in solution.

It is still another object of this invention to provide a simple and effective method of selectively concentrating the cations contained in a solution of neutron irradiated uranium by means of chromatographic adsorption under conditions such that the final product is free from large volumes of liquid.

It is still another object of this invention to provide a method of separating fission products from a solution containing the same solely by adsorption and capable of remote control without the necessity of handling large volumes of liquid.

It is a further object of this invention to provide a remotely controllable adsorption method of separating

fission products from a solution containing the same which may be employed in conjunction with other separation methods for separating the components of a neutron irradiated uranium mass while avoiding the necessity of handling extremely large volumes of liquid.

These and other objects of this invention will become apparent to those skilled in the art upon becoming familiar with the following description.

We have found that the volume of liquid to be handled in chromatographic adsorption processes of the type described above may be greatly reduced by a process which involves passing the solution containing the components to be separated through a body of adsorbent under conditions favoring the adsorption of the desired component, eluting the desired component from the adsorbent, converting the eluate to a condition favoring the adsorption of the desired component therefrom, adsorbing the converted eluate upon at least one smaller body of adsorbent and eluting the desired component from the smaller body of the adsorbent.

Our invention may be more readily understood by reference to the accompanying drawings in which:

Figure 1 is a diagrammatic view of an apparatus which may be utilized in the practice of our invention.

Figure 2 is a diagrammatic view of an apparatus for utilizing our invention in the separation of the constituents of a complex radioactive mixture such, for example, as a solution of neutron irradiated uranium.

Referring to the drawing, with particular reference to Figure 1, the system comprises feed line **1**, controlled by valve **2**, which passes into tank **3** to the upper portion of which are connected line **4**, controlled by valve **5**, and line **6**, controlled by valve **7**. Passage from the bottom of tank **3** is provided by line **8**, controlled by valve **9**, which line connects to the upper portion of column **10** containing an adsorbent **11**. To the upper portion of column **10** are also connected line **12**, controlled by valve **13**, and line **14**, controlled by valve **15**. Line **16** connects the lower portion of column **10** to line **17**, controlled by valve **18**, and to line **19**, controlled by valve **20**, line **19** passing into header **21** which has connected to the upper portion thereof line **22**, controlled by valve **23**, and line **24**, controlled by valve **25**. The bottom of header **21** is connected to the upper portion of column **28** by means of line **26**, controlled by valve **27**. Column **28** contains a suitable adsorbent **29** which may be the same as the adsorbent utilized in column **10**, or if desired, may be of a different type. To the top of column **28**, are connected line **30**, controlled by valve **31**, and line **32**, controlled by valve **33**. The bottom of column **28** has connected thereto line **34** which connects to line **35**, controlled by valve **36**, and to line **37**, controlled by valve **38**.

In operation of the system above described, valve **2** is opened and the solution to be separated is led through line **1** into tank **3**, valve **9** in line **8** being closed. In tank **3**, the condition of the solution may be adjusted to the desired state by the admission of reagent in line **6**, controlled by valve **7**. Agitation of material in tank **3** may be provided by means of air introduced through line **4**, controlled by valve **5**, and when the solution has reached the desired condition, the air may be utilized to force the solution out of tank **3** through line **8**, controlled by valve **9**.

When the solution has reached the desired condition, valve **9** is opened, and the solution passes through line **8** into column **10** wherein the desired components are adsorbed upon the adsorbent bed **11**. The unadsorbed material passes through lines **16** and **17** to disposal, valve **18** being open, and valve **20** in line **19** being closed. After allowing sufficient time for the desired adsorption to take place, elution of the desired components is accomplished by passing a suitable reagent through line **12** controlled by valve **13**, and with valve **18** in line **17** closed and valve **20** in line **19** open, the eluate from column **10** is passed into header **21** and is there conditioned by the admission of reagent through line **22**, controlled by valve **23**, so as to render the desired components capable of being adsorbed in column **28** by adsorbent **29**. If desired, agitation may be provided by admission of air into header **21** through line **24**, controlled by valve **25**. Upon reaching this desired condition, valve **27** in line **26** is opened and the air admitted through line **24** controlled by valve **25** is utilized to force the solution in header **21** through line **26** into column **28** wherein the desired adsorption takes place.

After a suitable period of time depending, among other things, upon the material under treatment, the desired component, the body of adsorbent, if desired, may be washed with water which is fed through line **32** controlled by valve **33**, the washings passing through line **34** and line **36** controlled by valve **35** to disposal thereby eliminating from the system any undesired material. Upon removal of this undesired material, the condition of the adsorbed material is changed by the admission of reagent through line **30** controlled by valve **31**, and with valve **35** in line **36** closed and valve **38** in line **37** open, the desired components are eluted by reagent from the system.

A system such as that described above may be utilized in separating individual components from a solution containing the same and results in a substantial reduction in volume of the liquid which must be handled during the operation of the process. Such a system is also capable of separating groups of components from a solution containing the same together with other components.

Our invention may be readily understood by reference to the following specific examples.

EXAMPLE I

A 10% uranyl nitrate hexahydrate solution containing yttrium activity as the only radioactive component was passed through a column containing an ion exchange resin characterized by having a plurality of $—CH_2SO_3H$ groups. Dilute H_2SO_4 was added to remove uranium. The radioactive yttrium tracer was eluted from the resin by tartaric acid at a pH of 2.7. The eluate was next acidified to the pH of a 5% tartaric acid solution (1.6) and readsorbed on to a column of $\frac{1}{10}$ the capacity of the original column. The adsorbent was then washed with water to remove the tartaric acid and the yttrium activity eluted with 3 to 6 N hydrochloric acid.

EXAMPLE II

A solution comprising radioactive barium tracer was passed into a 20 milliliter column resulting in the adsorption thereon of the barium. The barium was eluted from the 20 milliliter column in 40 milliliters of 5% citrate at a pH of 6.0. The resulting solution was diluted and acidified to 400 milliliters of ½% citrate at at pH of 2.5 and was run through a 2 milliliter capacity ion exchange column in 20 to 80 minutes. The barium was subsequently eluted from the 2 milliliter column in about 4 milliliters of 5% citrate at a pH of 6.0. The cycle of elution, dilution, acidification, readsorption, and re-elution therefore meet in a concentration of ten fold with respect to the barium.

While the above examples illustrate the embodiments of our invention wherein a particular radioactive material is specifically obtained, our invention may be applied in a form such as to recover the individual fission products from a solution of neutron irradiated uranium. In such an embodiment, the conditions of adsorption and elution are controlled and a sufficient number of columns are employed so as to obtain the individual fission products, or if desired, groups of individual fission products in a highly concentrated form.

As illustrative of a process involving the separation of fission products from a solution of neutron irradiated uranium, the fission products in a 10% solution of uranyl nitrate hexahydrate may be adsorbed in a large

column, the uranyl ion may be removed with a suitable reagent such as dilute sulfuric acid, the zirconium and columbium, rare earths, and alkaline earths may be successively eluted from the column and thereafter further separated and purified as fission products from these groups. The first three groups may be removed successively from the first column and the final separation may be made in the third column. There may be provided a separate fourth column which may be utilized for each element being recovered.

A system which may be utilized in the separation of fission products contained in a neutron irradiated uranium mass in accordance with our invention is illustrated in Figure 2. Referring to Figure 2, the entire system is inclosed in a cell, because of the extreme radioactivity of the material under process, the cell roof being designated as 21 through which pass the numerous lines necessary for operation of the system as pointed out below. The feed line 22 controlled by valve 23 is connected to the upper portion of make-up tank 24. Also connected to the upper portion of tank 24 and extending through cell wall 21 are vent line 25, controlled valve 26, air line 27, controlled by valve 28, reagent line 29, controlled by valve 30, and water line 31, controlled by valve 32. Make-up tank 24 is connected at its lower portion by means of line 33 controlled by valve 34 to the upper portion of adsorbent column 35 which contains a suitable adsorbent 36. To the top of adsorbent column 35 is also connected water line 37, controlled by valve 38. Passage from the bottom of adsorbent column 35 is provided by line 39. Line 39 leads through shielded ionization chamber 41 into mixing header 42. Mixing header 42 has connected to the top thereof vent line 43 and reagent line 45 controlled by valves 44 and 46 respectively, located outside of the cell. The lower portion of mixing header 42 is connected to a three-way piping system which may consist of line 47, controlled by valve 48, which leads into the top of column 49, line 50, controlled by valve 51, which leads to another column, not shown, which may be utilized if separation of the rare earth elements is desired, and line 52, controlled by valve 53, which leads to mixing header 54.

Column 49 contains a suitable adsorbent 55 and is connected from the lower portion thereof by means of line 60 through shielded ionization chamber 61 to the upper portion of mixing header 54. Connected to the upper portion of column 49 is water line 95, controlled by valve 96. Connected to the upper portion of mixing header 54 are vent line 62, controlled by valve 63, and reagent line 64, controlled by valve 65.

The lower portion of header 54 is connected to a two-way piping system comprising line 66, controlled by valve 67, which leads to disposal, and line 68, controlled by valve 69, which leads to the upper portion of column 70 containing a suitable adsorbent 71. To the upper portion of column 70 is also connected water line 97, controlled by valve 98, and the lower portion of column 70 is connected to line 72 which passes through shielded ionization chamber 73 to the top of header 74 which also has connected to the upper portion thereof reagent line 75, controlled by valve 76, vent line 77, controlled by valve 78, and air line 79, controlled by valve 80. The lower portion of header 74 is connected to a two-way pipe system which consists of line 81, controlled by valve 82, which leads to disposal, and line 83, controlled by valve 84, the outlet which is positioned above a merry-go-round column selector 85.

Column selector 85 operated by means not shown contains a plurality of small columns 86 each of which contains an adsorbent 87. Disposed above column selector 85 is the outlet of reagent line 88, controlled by valve 89. By rotation of column selector 85, the various columns may be successively disposed simultaneously beneath both the outlet of line 83 and the outlet of line 88. Each of the columns 86 has a discharge line 90, the outlet of which is positioned above funnel 90 which discharges into shielded ionization chamber 91. To the bottom of shielded ionization chamber 91 is connected line 92, the other extremity of which is positioned above a storage selector comprising a plurality of funnels 93 semi-circularly disposed in a rack and connected to a plurality of storage chambers 94. By rotating the storage selector approximately 180° about the axis of the outlet of line 92, the discharge from the ionization chamber may be collected in the desired storage chamber.

The operation of the system described in Figure 2 will be illustrated by reference to the separation of the components of a solution of neutron irradiated uranium. However, it is to be understood that this system may be utilized for the separation of the components of a wide variety of solutions.

The solution of neutron irradiated uranium is passed through line 22 controlled by valve 23 into make-up tank 24. In make-up tank 24 the solution is adjusted to the desired condition by admission of reagent through line 29 controlled by valve 30. If desired, agitation may be provided by opening valve 28 in line 27 thereby admitting a stream of air into the material contained in make-up tanke 24. When the desired condition of the solution in make-up tank 24 has been attained, valve 34 in line 33 is opened and the thus conditioned solution passes by gravity into column 35 wherein the desired adsorption upon adsorbent 36 takes place. Flow through column 35 is controlled by means of valve 26 in vent line 25 as well as by means of valve 34 in line 33. The unadsorbed portion of the solution passes from column 35 through line 39, shielded ionization chamber 41 and into mixing header 42. If further treatment of the effluent from column 35 is desired, it is caused to flow from header 42 through line 50 controlled by valve 51, to one or more other columns (not shown), valve 48 in line 47 and valve 53 in line 52 being closed.

If no further treatment of the solution in header 42 is desired, valves 51 and 47 are closed and valve 53 in line 52 is opened thus allowing the solution to flow through line 52 and mixing header 54 to line 66 to disposal, valve 67 in line 66 being open and valve 69 in line 68 being closed.

The adsorbed material in column 35 is then eluted by the admission of an eluting agent through line 37 controlled by valve 38 the eluate passing through line 39 and shielded ionization chamber 41 to mixing header 42 wherein the condition of the eluate is adjusted to a state such that the desired components may be adsorbed by adsorbent 55 in column 49 which column has a smaller capacity than column 35.

Upon reaching the desired condition, the eluate is allowed to flow into column 49, valves 51 and 53 being closed and valve 47 being open. Unadsorbed material is withdrawn from column 49 through line 60 and ionization chamber 61 through mixing header 54 from which it passes to disposal through line 66. The adsorbed material in column 49 is then eluted therefrom by the admission of reagent through line 95 controlled by valve 96 and passes through line 60, ionization chamber 61 into mixing header 54 where its condition is again adjusted by the admission of the reagent through line 64 controlled by valve 65.

Upon reaching the desired condition, the solution in mixing header 54 is passed through line 68 controlled by valve 69, valve 67 being closed, into column 70 wherein the desired components are adsorbed by adsorbent 71, the unadsorbed material passing through line 72 and shielded ionization chamber 73 into mixing header 74 and thence to disposal through line 81. The adsorbed material in column 70 is eluted by admission of reagent through line 97 controlled by valve 98, and passed through shielded ionization chamber 73 into mixing header 74 wherein the solution is successively treated with reagents admitted through line 77, controlled by

valve 78, and the desired components are selectively collecting by passing the conditioned solution through line 83, controlled by valve 84, to the desired columns contained on merry-go-round selector 85. The desired components are adsorbed by the adsorbents 87 and selectively eluted therefrom by the admission of eluting agent through line 88, the eluate being collected by a funnel 90 which feeds into shielded ionization chamber 91. From shielded ionization chamber 91 the eluate is carried by line 92 and collected in the desired storage chamber 94 by means of the desired funnel 93.

While the above system has been described with reference to the collection of desired components in storage chamber 94 after elution from columns 86, if desired, certain of the components may be recovered by controlling the condition of adsorption and elution by each of the larger columns 35, 49 and 70.

The purpose of the shielded ionization chambers is to measure the activity of the effluent solutions from the various columns, and, these chambers are connected to recording instruments located outside of the cell thereby enabling the operator to determine the activity of the solutions passing through the chambers.

In lieu of a single reagent line for each of the columns and mixing header as shown in Figure 2, a plurality of reagent lines may be utilized for the separate addition of the various reagents required, the number of reagents depending upon the material under treatment.

The conditions necessary for selective adsorption and selective elution may vary depending upon the adsorbent, the solution under treatment and the component or components desired to be recovered. Generally speaking, when processing solutions of neutron irradiated uranium, the pH of the solution is adjusted to between about 1 and 3 during the adsorption steps and is adjusted to between about 3 and 6 during the eluting steps. The particular pH to be utilized varies depending upon the individual component to be recovered and the individual eluting agent.

A highly successful method of selectively eluting fission products involves the addition of carboxylic acids and salts thereof at controlled pH's. Examples of such eluting agents which may be employed are polycarboxylic acids and salts thereof such as oxalic acid, citric acid, tartaric acid, sodium citrate, sodium tartrate, ammonium citrate, ammonium tartrate, and the like. Ammonium salts of polycarboxylic acids such as ammonium citrate are particularly advantageous eluting agents for use in the chromatographic separation of the fission products present in a solution of neutron irradiated uranium when ion exchange resins of the type described above are employed.

The rate of flow of solution through the various columns and the rate of flow of eluting agents through the various columns depends, among other things, upon the size of the column, the particular adsorbent, the original solution passed through the column, and the components desired to be recovered. Generally speaking, the original solution is passed through the first column at a rate of flow of approximately 75 to 150 milliliters per minute when utilizing a column of approximately 6 liters' capacity. Particularly advantageous results may be obtained with such a column when the rate of flow is maintained at approximately 100 milliliters per minute. The same conditions generally apply for the passage of eluting agents through the initial column.

As the smaller columns are reached, it is advantageous to reduce the rate of flow of both material and eluting agent therethrough, this rate of flow depending upon the size of the particular column.

As illustrative of the treatment of a solution of neutron irradiated uranium for the recovery of particular fission products therefrom in accordance with our invention, the following example is given.

EXAMPLE III

25 liters of a 10% uranyl nitrate hexahydrate solution was passed through an adsorption column having a 6 liter capacity and containing an ion exchange resin characterized by having a plurality of ($—CH_2SO_3H$) groups. The rate of flow of the solution was maintained at approximately 100 milliliters per minute resulting in a through-put time of 250 minutes. After the 250 minute through-put period, 20 liters of 0.25 M H_2SO_4 was passed through the column at 200 milliliters per minute resulting in a 100 minute through-put time thereby removing from the column any UO_2^{++} ion which may have been adsorbed from the column. 10 liters of 0.5 M citrate at a pH of 2.4 was then passed through the column at a flow rate of 50 milliliters per minute resulting in a 200 minute through-put time. The resulting eluate was made acid with nitric acid and passed through a 100 milliliter column containing an adsorbent of the type utilized in the 6 liter column, the same flow rate being maintained. Following the passage of this eluate through the 100 milliliter column, 1 liter of 0.5 M citric acid was passed therethrough at a rate of 4 milliliters per minute, the resulting eluate made acid with nitric acid, and passed through a 5 milliliter resin adsorption column, the unadsorbed material passing off to disposal. Following this procedure, 1 liter of 0.5 M citrate at a pH of 2.4 was passed through the 100 milliliter column at a flow rate of 4 milliliters per minute and the eluate adjusted with nitric acid to a pH of 1.8 and passed through a second 5 milliliter adsorption column, the unadsorbed material being passed to disposal.

Through the first 5 milliliter column was then passed 25 milliliter of 0.01 M oxalic acid at a flow rate of 1 milliliter per minute, the eluate being collected in a storage container and identified as columbium activity.

Through the second 5 milliliter column was passed 50 milliliters of 0.5 M citric acid at a flow rate of 2.5 milliliters per minute and the affluent therefrom sent to disposal. Thereafter, 25 milliliters of 0.01 M oxalic acid was passed through the second 5 milliliter column at a flow rate of 1 milliliter per minute and the eluate passed into a storage container and identified as zirconium activity.

After the recovery of columbium and zirconium activity in the manner indicated above, 25 liters of 0.2 M citrate at a pH of 3.5 was passed through the 6 liter column at a flow rate of 100 milliliters per minute. The eluate was adjusted to a pH of 2.4 with nitric acid and passed through a 100 milliliter resin adsorption column with the unadsorbed material passing to disposal. Thereafter, 1 liter of 0.5 M citrate at a pH of 2.4 was passed through this 100 milliliter column and the effluent sent to disposal. Following this, 1 liter of 0.2 M citrate at a pH of 2.75 was passed through the 100 milliliter resin column at a flow rate of 4 milliliters per minute and the eluate adjusted to a pH of 2.4 by the addition of nitric acid and passed through a third milliliter resin adsorption column, the unadsorbed material being sent to disposal.

Thereafter 1 liter of 0.2 M citrate at a pH of 3.5 was passed through the 100 milliliter column at a flow rate of 4 milliliters per minute, the eluate adjusted by means of nitric acid to a pH of 2.75 and passed through a fourth 5 milliliter resin column, the effluent from the column being sent to disposal.

Through the third 5 milliliter resin column was then passed 50 milliliters of 0.2 M citrate at a pH of 2.4 at a flow rate of 2.5 milliliters per minute, the effluent being passed to disposal. The condition of the adsorbed material in the third column was then changed by the passage therethrough of 25 milliliters of 0.5 M HCl at a flow rate of 2.5 milliliters per minute. Thereafter, 25 milliliters of 6 M HCl was passed through the third resin column at a flow rate of 1 milliliter per minute and the eluate collected in a storage container and identified as yttrium activity.

Through the fourth 5 milliliter column was then passed 50 milliliters of 0.2 M citrate at a pH of 2.75 and at a rate of flow of 2.5 milliliters per minute, the effluent being sent to disposal. The adsorbed material in the fourth column was then conditioned by the passage therethrough by 50 milliliters of 0.5 M HCl at a flow rate of 2.5 milliliters per minute and was then eluated from the adsorbent by passage therethrough of 25 milliliters of 6 M HCl at a flow rate of 1 milliliter per minute, the eluate being collected in a storage container and identified as cerium activity.

Following the selective recovery of the above mentioned activity the 6 liter column was washed with 15 liters of 0.2 M citrate at a pH of 7.5 and at a flow rate of 100 milliliters per minute, the eluate being adjusted to a pH of 3.5 by means of nitric acid and diluted with 60 liters of water and then passed through a 300 milliliter resin adsorption column, the unadsorbed material passing to disposal. The condition of the adsorbed material in the 300 milliliter column was adjusted by passage therethrough by 3 liters of 0.2 M citrate at a pH of 3.5 and at a flow rate of 100 milliliters per minute, the effluent from the column being sent to disposal. Thereafter 1.5 liters of 0.2 M citrate at a pH 7.5 was passed through the 300 milliliter column at a flow rate of 75 milliliters per minute, the resulting eluate was adjusted by means of nitric acid by a pH 3.5, diluted with 1200 milliliters of water and passed through the 100 milliliter resin column, the effluent from this column being sent to disposal.

The 100 milliliter resin column was then washed with 1 liter of 0.2 M citrate at a pH of 3.5 and at a rate of flow of 10 milliliters per minute the washings being sent to disposal. Thereafter 1 liter of 0.2 M citrate at a pH of 4.8 was passed through the 100 milliliter column at 4 milliliters per minute, the first 400 milliliter of the resulting eluate was adjusted to a pH of 3.5 with nitric acid, diluted with 1600 milliliters of water and then passed into a first 10 milliliter resin adsorption column, the effluent being sent to disposal. The remaining eluate was adjusted to a pH of 3.5 with nitric acid and diluted with 2400 milliliters of water and passed into a second 10 milliliter column, the effluent of the second column being sent to disposal.

Returning to the first 10 milliliter column, the adsorbed material therein was washed with 50 milliliters of 0.2 M citrate at a pH of 3.5 and at a rate of flow of 2.5 milliliters per minute. Thereafter, the adsorbed material was washed with 50 milliliters of 0.5 M HCl at a rate of flow of 2.5 milliliters per minute. The adsorbed material was then eluted by passing through the column 30 milliliters of 6 M HCl at a rate of flow of 1 milliliter per minute. The eluate was collected in a storage container and identified as strontium activity.

The adsorbed material in the second 10 milliliter column was washed with 50 milliliters of 0.2 M citrate at a pH of 3.5 and at a rate of flow of 2.5 milliliters per minute and thereafter washed with 50 milliliters of 0.5 M HCl at a rate of flow of 2.5 milliliters per minute. The adsorbed material was then eluted from the column by passing therethrough 40 milliliters of 6 M HCl at a rate of flow of 1 milliliter per minute. The eluate was collected in a storage container and identified as barium activity.

While our invention has been described with reference to certain forms of apparatus, it is to be understood, of course, that the design of the particular columns may be varied depending upon the conditions obtaining during the treatment of the material under process. Generally speaking, two factors are to be considered in designing the various columns for use in the practice of our invention. The size of the first column is determined by the breakthrough curve for activity from a 10% uranyl nitrate hexahydrate solution containing the fission products. The sizes of the subsequent columns are determined by the volume reduction possible in each step. In determining the geometry of the columns (the height: diameter ratio for any given column, etc.), it is advantageous to consider two general factors, namely the optimum geometry for maximum volume reduction and the most practical geometry for construction and operation. For example, a very large height:diameter ratio which may improve the volume reduction would reduce the flow rate below a practical operation value. In addition, such columns might be too long to fit in the available space, remembering in dealing with radioactive solutions all operations are conducted within an inclosed cell provided to shield operators against the effects of radiation. Particularly advantageous results may be obtained when the columns are of such design to permit gravity flow of the material under treatment therethrough.

Although the system above described utilizes gravity for flowing the various materials through the columns, the material under treatment may be caused to flow through the columns by other means such as the pressure supplied by suitably positioned pumps.

Also, if desired, the number of components separated from the solution under process may be increased by recycling certain of the discarded effluents through the system or by increasing the number of columns in the system to further process certain of the effluents.

As pointed out above, while the pH for adsorption is, generally speaking, less than the pH for elution, the pH, in either instance, will depend on the particular cations to be adsorbed or desorbed. A volume reduction of at least ten-fold is generally always achievable by this invention. For instance, the size of the column containing the adsorbent bed may be reduced from 1 liter capacity to 100 cc. capacity. Since in each case, the adsorbent bed volume is directly proportional to the eluting agent volume, reducing the bed capacity by a factor of 10 also serves to reduce the volume of the eluting agent by the same factor.

Generally speaking, the invention is particularly adaptable to the separation of metal cations especially those cations which occur as fission products in the preparation of radioactivities either with or without added inactive carriers. The process of the invention is equally effective for the separation of mixtures of, or of individual fission products. Generally speaking, the preferred pH for the initial and eluting solution will depend on the acid used, on the adsorbent used, and on the cations to be adsorbed; ordinarily the adsorption solution will have a lower pH than the eluting solution.

In the practice of our invention, it is particularly advantageous to remove any excess acid such as tartaric or citric acid which may be adsorbed, particularly where tracer quantities are involved. Such a removal may be accomplished by washing the adsorbent with distilled water which procedure removes the excess acid without removing the desired cations.

When ammonium ion is present in the eluting agent or complexing agent, the adsorbate in the final column is contaminated therewith. Should removal of NH_4^+ be desired, it may be accomplished by washing the adsorbate with 3–6 N HCl. Such a procedure also removes other inactive cations such as iron, aluminum and the like which may be present in the final adsorbate.

An alternate procedure for removal of NH_4^+ is to remove the cations from the final body of adsorbent with 3–6 N HCl and thereafter destroy the NH_4^+ by the addition of aqua regia to the eluate.

The desired activity may be separated from the solvent by evaporating the liquid to dryness thus isolating the activity as the salt of the acid employed as a final eluting agent. When HCl is utilized, the activity is isolated as the cation chloride.

While the invention has been particularly described with reference to the separation of the components of a solution of neutron irradiated uranium, it is to be under-

stood that other types of solutions may be separated by means of the process of the invention. For example, the invention may be applied to the separation of rare earths as well as to the separation of U^{233} from neutron irradiated thorium. The invention may also be applied to the separation of cyclotron bombarded materials.

In lieu of utilizing a solution of neutron irradiated uranium as starting material in the practice of our invention, an extract of such a solution may be employed such as the water solution of fission products resulting after the extraction of uranium by means of a solvent such as ether. In such an extraction process, the uranium present in a uranyl nitrate solution is extracted with a suitable solvent such as ether. The remaining liquid comprising a nitric acid solution is contacted with water to obtain an aqueous solution of fission products. When such an aqueous solution is processed in accordance with our invention, the larger columns in the system illustrated in Fig. 2 may be bypassed and the separation begun by adsorption on a smaller column.

While the above description makes particular mention of the separation of cations, the process of the invention may also be utilized in the separation of anions. One method of separating anions is that involving the utilization of an adsorbent selective for anions such as an anion exchange resin. In some instances, the anions of the desired components may be converted to cations and processed in a manner similar to that above described. The process of our invention enables a change of solvent for the desired components by appropriate manipulation of the system. For example, the eluting agent may be changed to obtain the desired solution of activity.

The process of our invention may also be utilized as a method of preparing pure isotope products either active or inactive. For example, a parent element may be separated by our method and stored for a sufficient time to produce a daughter element. Then the daughter element may be recovered by means of our process.

In the specification and claims the following terms have the following meanings.

The term "effluent" or its equivalent is intended to include any material coming off of the columns.

The term "eluate" or its equivalent is intended to include any effluent bearing a desired product from a column.

The term "eluting agent" or its equivalent is intended to include a material which removes activity from a column.

The term "adsorption" is utilized in referring to removal of components from the solution. It is to be understood, however, that the invention is not to be limited in any sense by the theory upon which the process is based and that this term is used as it is generally employed in the art of chromatographic separation.

While the invention has been described with reference to certain particular embodiments and with reference to certain specific examples, it is to be understood that the invention is not to be limited thereby. Therefore, changes, omissions, and/or additions may be made without departing from the spirit of the invention as defined in the appended claims which are intended to be limited only as required by the prior art.

We claim:

1. A process for concentrating uranium fission product metal cations from an original volume of aqueous solution containing the same, which comprises contacting said solution with a body of ion-exchange adsorbent to effect adsorption of said cations thereupon, then contacting the fission-product bearing adsorbent with an aqueous solution of an agent selected from the group consisting of carboxylic acids and salts thereof to thereby elute said fission product cations in a volume of eluate smaller than said original volume, thereupon substantially acidifying the resulting eluate without increasing its volume to the magnitude of said original volume, thereafter contacting the acidified eluate with a smaller body of ion-exchange adsorbent to effect readsorption of said cations thereupon.

2. In a process for separating uranium fission product metal cations from an initial aqueous solution containing the same comprising adsorption of said cations upon a body of ion-exchange adsorbent, the improvement method for increasing the solution concentration of said fission product cations with respect to their concentration in said initial solution, which comprises contacting the resulting fission-product-bearing adsorbent with an aqueous solution of an agent selected from the group consisting of carboxylic acids and salts thereof to thereby elute said fission-product cations in a volume of eluate smaller than that of said initial solution, then substantially acidifying the resulting eluate without increasing the volume to the magnitude of that of said initial solution, thereafter contacting the acidified eluate with a smaller body of ion-exchange adsorbent to effect readsorption of said cations thereupon, and subsequently contacting the resulting fission-product-bearing smaller body of adsorbent with an agent selected from the group consisting of carboxylic acids and salts thereof to thereby elute said fission product cations in a volume of elute even smaller than the aforesaid smaller volume of eluate.

3. The process of claim 2 wherein said agent is a polycarboxylic acid.

4. The process of claim 2 wherein said agent is a polycarboxylic acid salt.

5. In a process for separating uranium fission product metal cations from an initial aqueous solution containing the same comprising adsorption of said cations from said solution upon a body of ion-exchange adsorbent, a method for increasing the solution concentration of said cations with respect to their concentration in said initial solution, which comprises contacting the resulting fission-product-bearing adsorbent with an aqueous solution having a pH within the approximate range pH 3 to 6 of a polycarboxylic acid salt to thereby elute said fission product cations in a volume of eluate smaller than that of said initial solution, then acidifying the resulting eluate to the approximate range of pH 1 to 3 without increasing its volume to the magnitude of that of said initial solution, thereupon contacting the acidified eluate with a smaller body of ion-exchange adsorbent to effect readsorption of said cations thereupon, and subsequently contacting the resulting fission-product-bearing smaller body of adsorbent with an aqueous solution having a pH maintained within the approximate range of pH 3 to 6 of a polycarboxylic acid salt to thereby elute said fission product cations in a volume of eluate even smaller than the aforesaid smaller volume of eluate.

6. The process of claim 5 wherein said polycarboxylic acid salt is an ammonium salt of a polycarboxylic acid.

7. The process of claim 5 wherein said polycarboxylic acid salt is ammonium citrate.

8. The process of claim 5 wherein said ion-exchange adsorbent is an inert organic material containing free sulfonic acid groups.

9. The process of claim 5 wherein said ion-exchange adsorbent is a granulated resin having a plurality of $-CH_2SO_3H$ groups.

10. In a process for separating rare earth cations from an initial aqueous solution containing the same comprising adsorption of said cations from said solution upon a body of ion-exchange adsorbent, a method for increasing the solution concentration of said cations with respect to their concentration in said initial solution, which comprises contacting the fission-product-bearing adsorbent with an aqueous solution having a pH within the approximate range pH 3 to 6 of a polycarboxylic acid salt to thereby elute said rare earth cations in a volume of eluate smaller than that of said initial solution, then acidifying the resulting eluate to the approximate range of pH 1 to 3 without increasing its volume to the magnitude of that of said initial solution, there-

upon contacting the acidified eluate with a smaller body of ion-exchange adsorbent to effect readsorption of said cations thereupon, and subsequently contacting the resulting fission-product-bearing smaller body of adsorbent with an aqueous solution having a pH maintained within the approximate range of pH 3 to 6 of a polycarboxylic acid salt to thereby elute said rare earth cations in a volume of eluate even smaller than the aforesaid smaller volume of eluate.

11. In a process for separating yttrium cations from an initial aqueous solution containing the same in trace concentration comprising adsorbing said cations upon an ion-exchange adsorbent resin having a plurality of $-CH_2SO_3H$ groups, a method for increasing the solution concentration of said yttrium cations with respect to their concentration in said initial solution, which comprises contacting the resulting yttrium-bearing adsorbent with an aqueous solution having a pH of 2.7 of tartaric acid to thereby elute said yttrium cations in a volume of eluate smaller than that of said initial solution, then acidifying resulting eluate to pH of approximately 1.6 without increasing its volume to the magnitude of that of said initial solution, thereupon contacting the acidified eluate with a smaller body of ion-exchange adsorbent resin having a plurality of $-CH_2SO_3H$ groups to effect readsorption of said cations thereupon, and subsequently contacting the resulting yttrium-bearing smaller body of adsorbent with approximately 3 to 6 normal hydrochloric acid to thereby elute said yttrium cations in a volume of eluate even smaller than the aforesaid smaller volume of eluate.

12. In a process for separating barium cations from an initial aqueous solution containing the same in trace concentration comprising adsorbing said barium cations upon an ion-exchange adsorbent resin having a plurality of $-CH_2SO_3H$ groups, a method for increasing the solution concentration of said barium cations with respect to their concentration of said initial solution, which comprises contacting the resulting barium-bearing adsorbent with an aqueous solution having a pH of approximately 6 of approximately 5% ammonium citrate to thereby elute said barium cations in a volume of eluate smaller than that of said initial solution, thereafter diluting and acidifying the resulting eluate to an approximately ½% citrate concentration and a pH of approximately 2.5, thereupon contacting the acidified eluate with a smaller body of ion-exchange adsorbent resin having a plurality of $-CH_2SO_3H$ groups to effect readsorption of said cations thereupon, and subsequently contacting the resulting barium-bearing smaller body of adsorbent with an aqueous solution having a pH of approximately 6 of approximately 5% ammonium citrate to thereby elute said barium cations in a volume of eluate even smaller than the aforesaid volume of eluate.

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