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SEPARATION OF RADIOACTIVE COLUMBIUM TRACER

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This invention relates to a method of processing material containing radioactive columbium values in small amount, for the separation of the columbium activity from extraneous matter such as substances of the kind present in solutions of neutron irradiated uranium, for example, for the separation of columbium values from plutonium values, from other fission product values, and especially from tellurium values. More particularly, this invention relates to a method of separating tracer quantities of columbium activity from solutions containing the same and also containing tellurium activity by carrying said columbium activity out of solution on a carrier and separating said columbium activity from the carrier.

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 "columbium values" is intended to include columbium 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 "columbium activity" as employed herein is intended to include radioactive columbium 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 electromagnetic radiation similar to X-rays but with a short 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 a 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 corresponding natural elements 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 emission 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 decay chain 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 ir-

radiation 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 excellent sources of radioactivity which may be utilized, among other things, in various fields such as medicine and metallurgy.

Among the fission product values which it is desirable to isolate is radioactive columbium. It has been found that columbium is present in the above described group of radioactive fission products in comparatively low proportion by weight. Since the percentage of fission products in the overall mass is extremely small, it can be readily seen that the quantity of columbium present in the overall mass to be treated is such as to be considered a tracer quantity. In addition to the difficulties already mentioned in connection with the separation of fission products, the separation of carrier-free columbium activity is further complicated by the fact that columbium is generally associated with tellurium in a neutron irra-

diated uranium mass. This association renders the isolation of columbium activity extremely difficult in that tellurium activity is carried down from solution together with the columbium activity by all of the preferred known carriers for columbium activity.

It is an object of this invention to provide a new method for the separation and recovery of radioactive columbium activity.

Another object of this invention is to provide a process for separating radioactive columbium values from an irradiated mass containing plutonium values as well as other fission product values.

Still another object of this invention is to provide a method of preparing carrier-free columbium activity.

It is a further object of this invention to provide a process for the isolation of tracer quantities of columbium activity which may be conveniently operated under conditions of remote control.

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

We have found that solutions containing tracer quantities of columbium activity may be treated to isolate said columbium activity by a process involving the removal of columbium activity by carrying the same on a carrier such as manganese dioxide and separating the tellurium activity from other constituents in the form of elemental tellurium or in a similar readily removable reduced state.

The columbium-activity-containing solutions which may be treated in accordance with our invention may be of any type. However, the invention is particularly adaptable for the recovery of tracer quantities of columbium activity from solutions containing the same. In other words, our invention is particularly adapted to the recovery of columbium activity from extremely dilute solutions thereof. In this connection, the invention is paraticularly adapted to the treatment of the usual columbium-activity-containing solutions grenerally encountered. Among the most common columbium-activity-containing solutions is that resulting from the dissolution of neutron irradiated uranium following the removal thereof from the irradiation zone. Following the irradiation of metallic uranium, it is generally the practice to dissolve the irradiated uranium in nitric acid, thereby producing a solution of uranium nitrate hexahydrate which is commonly referred to as UNH solution. This UNH solution contains in addition to plutonium values, values of the numerous fission products above described, including columbium values. Our invention is particularly suited for the removal of columbium activity from such solutions.

In certain processes for the separation of the numerous constituents of neutron irradiated uranium, it is the practice to obtain an ether extract of the above-mentioned UNH solution. In this extraction the ether layer contains the preponderant portion of the uranium values and the water layer contains the preponderant portion of the fission product values including columbium and tellurium values. The water layer from such an extraction process may be treated in accordance with our invention to obtain carrier-free columbium values therefrom. Although, generally speaking, the quantity of columbium values which may be present in the ether layer resulting from such a process is such as to be considered insignificant, if desired, the ether layer may be treated in accordance with our invention to recover therefrom any radioactive columbium values which may be present therein. When treating the ether layer, it is advantageous to evaporate a substantial quantity of the ether before treatment in accordance with our process.

It is also possible to utilize our procedure for the separation of columbium activity from any of the suitable by-product filtrates which are obtained in the chemical separation of plutonium values from neutron irradiated uranium.

It has been found that solutions of the types above described, containing columbium activity, may be acidified to the desired normality with a suitable inorganic acid such as nitric acid, sulfuric acid, perchloric acid and the like, and thereafter contacted with a columbium activity carrier such as MnO_2, TiO_2, SiO_2 and the like, thus forming a precipitate which carries the columbium activity together with any tellurium activity which may be present from the solution.

In the practice of our invention, solutions containing columbium activity which also contain tellurium activity are treated either prior to or after the carrying procedure in such a manner as to separate the tellurium activity and thereby enable the recovery of pure, carrier-free, columbium activity. Generally speaking, we have found that particularly advantageous results may be obtained when tellurium activity is separated from the solution under treatment prior to the columbium activity carrying step.

In one modification of our invention, which involves the removal of tellurium activity after carrying of columbium and tellurium activities, a solution containing columbium activity in tracer quantity is acidified with a suitable inorganic acid. In the acidification of the columbium-activity-containing solution, it is particularly advantageous to adjust the acidity of the solution to less than 16 N and preferably between 10 and 16 N. In this connection the conditions followed in this modification of the present process are such as make highly undesirable the utilization of acids yielding the chloride ion, such as HCl. Therefore, the preferred acids for use in the acidification step of our process are selected from the group consisting of inorganic acids other than HCl. These acids may also be classified as inorganic acids incapable of yielding chloride ion under the conditions obtaining. Nitric acid is advantageously utilized in one modification of our invention.

Following the adjustment of the solution to the desired acidity, the solution is contacted with a carrier for columbium and tellurium activities. The carrier precipitate obtained is dissolved and a carrier for elemental tellurium, advantageously inactive tellurium values such as H_2TeO_3, H_2TeO_4 and the like, is added. The solution is then contacted with a reducing agent selective for tellurium values, such as zinc, and the resulting precipitate of elemental inactive tellurium carries down the radioactive tellurium. After separation of the elemental tellurium from the solution, the remaining solution is contacted with a suitable columbium activity carrier, forming a carrier precipitate which may be dissolved and isolated from the columbium activity thereby yielding a solution in which columbium ions are the only radioactive metal ions.

In the phase of this modification our invention involving the addition of carrier and reducing agent, tellurium activity carrier may be added after the addition of the reducing agent, if desired. Generally speaking, however, it is advantageous to add the reducing agent simultaneously with the tellurium activity carrier or following the addition of the carrier. The same principles apply throughout the operation of our process. In other words, in those steps involving the addition of carrier and reducing agent, advantageous results may be obtained by adding the reducing agent after or simultaneously with the addition of the carrier. In some instances, however, it may be desirable to add the reducing agent prior to the addition of carrier.

In the final isolation of radioactive columbium values in accordance with our invention, particularly advantageous results may be obtained when utilizing basic ferric acetate to carry the columbium from the solution. Basic ferric acetate carries columbium activity from the solution without carrying manganese values. The ferric

ion may be readily separated from columbium activity by dissolving the basic ferric acetate carrier precipitate in hydrochloric acid, advantageously 8 N hydrochloric acid, and extracting the ferric ion from the solution thus obtained by means of ether. The remaining solution contains carrier-free radioactive columbium ions as the only metal ions present.

In a particularly advantageous modification of our invention, inactive tellurium ion is added to an acid solution, advantageously a hydrochloric acid solution, of oxalate-complexed columbium activity tracer prior to the columbium activity carrying step. A suitable reducing agent for tellurium activity is then added to the solution and the tellurium values are separated therefrom in a reduced insoluble form such as elemental tellurium, a compound of tellurium insoluble under the conditions obtaining, and the like. The remaining solution is then treated with a carrier, preferably manganese dioxide, to selectively remove radioactive columbium activity, and the resulting carrier precipitate is dissolved and treated in any suitable manner to obtain a solution of pure carrier-free columbium activity. Treatment with solid basic ferric acetate followed by extraction of ferric ion is a particularly advantageous method of recovering carrier-free columbium activity.

In this particular modification of our invention, any reducing agent which selectively reduces tellurium values to elemental tellurium or other insoluble forms under the conditions obtaining may be employed. Examples of such reducing agents are inorganic reducing agents, such, for example, as sulfur dioxide, hydrogen sulfide, and hydrazine.

While particularly advantageous results have been obtained in the practice of this modification of our invention utilizing manganese dioxide to carry the columbium activity from the solution free from tellurium values, other carriers for columbium activity may be utilized such as titanium dioxide and silicon dioxide.

In this modification of our invention, it is also possible to remove any molybdenum values which may be present in the solution under treatment. The removal of molybdenum values may be accomplished in a variety of ways, preferably by reduction to an insoluble state. Among the preferred methods of removing molybdenum values is that involving the addition of inactive molybdenum values to the solution together with the inactive tellurium values, and removing the molybdenum values prior to the carrying step. A particularly advantageous method of removing molybdenum values comprises adding an organic compound such as alpha benzoin oxime to the solution to precipitate molybdenum values as the insoluble molybdenum organic compound.

Another method of removing molybdenum values involves the addition of hydrogen sulfide thereby precipitating molybdenum sulfide which may be readily separated from the solution.

In the practice of our invention, the carriers employed for removing columbium activity may be either externally formed or formed in the solution. When utilizing externally formed carriers, it is particularly advantageous to conduct this step of our process at room temperature. However, if desired, other temperatures may also be employed. Particularly advantageous results have been obtained in the practice of our invention by carrying columbium activity on a carrier formed directly in the columbium-activity-containing solution. In this modification of our invention, which utilizes internally formed carrier, advantageous results have been obtained when conducting this carrying step at a temperature of from approximately 75° C. to approximately 110° C. It is generally preferable to operate at a temperature approximating the boiling point of the solution under treatment.

When utilizing externally formed manganese dioxide as a carrier, advantageous results have been obtained by employing such a carrier prepared by the oxidation of manganese nitrate to manganese dioxide by means of potassium chlorate in nitric acid. For example, a 20 milliliter solution of 50% manganese nitrate may be adjusted to 10 N with HNO_3 and the resulting mixture heated nearly to the boiling point. Forty grams of potassium chlorate may then be added in small batches and the resulting manganese dioxide suspension digested until most of the chlorine dioxide has been expelled. The manganese dioxide suspension may then be filtered through a suitable device such as a sintered glass filter funnel and the precipitate may be washed with water, alcohol and ether. The resulting manganese dioxide slurry may then be stored until used. Other methods of preparing manganese dioxide known to the art may of course be utilized in the preparation such slurries as are used in that modification of our invention which utilizes an externally prepared manganese dioxide.

The silicon dioxide and titanium dioxide which may be utilized in certain modifications of our invention may also be prepared in a number of ways. For example, silicon dioxide may be formed by adding sodium silicate solution to the nitric acid solution containing columbium activity. Titanium dioxide may be prepared by hydrolyzing titanium tetrachloride, washing, and adding the resulting slurry to the solution under treatment for the isolation of columbium activity. As in the case with manganese dioxide, both externally and internally formed carriers of this type may be utilized.

Generally speaking, the quantity of carrier added to solutions containing columbium activity in accordance with our invention is comparatively small. For instance, a fraction of a gram of carrier per liter of liquid under treatment is usually sufficient to accomplish the desired result. However, if desired, up to 5 grams per liter may be employed.

The process of our invention may be more readily understood by reference to the following specific examples:

EXAMPLE I

A solution containing radioactive columbium activity was made 10 N in HNO_3. Ten milligrams of Mn^{++} carrier and 1 gram of $KClO_3$ were added. The mixture was then heated cautiously to boiling. The gentle boiling was continued for 2–3 minutes to coagulate completely the precipitate of MnO_2. The precipitate was centrifuged, washed with 10 milliliters of 1 N HNO_3 and dissolved in 1–2 milliliters of 6 N HCl containing one drop of 30% H_2O_2. The resulting solution was then boiled nearly to dryness to expel excess H_2O_2 and was then taken up in 10–15 milliliters of 3 N HCl. Ten milligrams of Te carrier in the form of H_2TeO_4 and 0.5 gram of metallic zinc (20 mesh) were then added. The mixture was boiled gently until the zinc was completely dissolved and the precipitate of Te well coagulated. The Te was filtered out and discarded. The filtrate was evaporated nearly to dryness and then fumed nearly to dryness 2 or 3 times with a few milliliters of concentrated HNO_3 to remove the HCl. The residue was taken up in 10–15 milliliters of 10 N HNO_3, one gram of $KClO_3$ was added, and the solution was boiled gently for 2–3 minutes to reprecipitate the MnO_2. The precipitate was centrifuged and then dissolved in 1–2 millilters of 10 N HNO_3 containing 1 drop of 30% H_2O_2. Ten milliliters of 10 N HNO_3 were added, and the solution was boiled with 1 gram of $KClO_3$ to reprecipitate the purified MnO_2.

The precipitate thus obtained was centrifuged and dissolved in 10 milliliters of water containing 0.5 milliliters of 6 N HNO_3 and 1 drop of 30% H_2O_2. Five milligrams of Fe carrier was added, and the solution was boiled with a drop of liquid bromine until excess bromine was expelled. One milliliter of 3 M ammonium acetate was then added to the solution which was thereafter heated nearly to boiling, and 6 N NH_4OH was added dropwise

until a precipitate of basic ferric acetate was formed.

This precipitate was centrifuged and dissolved in 0.5 milliliter of 6 N HNO_3, 10 milliliters of water and 1 milliter of 3 N ammonium acetate was added. After this addition, the solution was heated and basic ferric acetate was reprecipitated by the dropwise addition of 6 N NH_4OH.

This precipitate was centrifuged, dissolved in 10 milliliters of 8 N HCl, and boiled for a minute with a drop of liquid bromine. The solution was then extracted three times with 10 milliliter portions of isopropyl ether in a separatory funnel. The aqueous phase was evaporated nearly to dryness to expel the ether, and diluted to the desired volume. At this point, the only metal ions contained in solution are those of radioactive columbium.

Yields of from 40–85% of radioactive columbium have been obtained by following the procedure of this example.

EXAMPLE II

To a suitable volume such as 5 to 100 milliliters of a fission product concentrate obtained by the ether extraction of UNH solution were added 10 milligrams of tellurium carrier as H_2TeO_3 and 10 milliliters of concentrated HCl. The solution was evaporated to approximately 2 milliliters. In this connection, evaporation to dryness was avoided in order to prevent the loss of columbium activity on the walls of the container. A second 10 milliliter portion of concentrated HCl was added and the solution again evaporated to about 2 milliliters. To the residual solution was added 20 milliliters of 3 M HCl, 2 milliliters of saturated oxalic acid and the resulting solution was heated to boiling. SO_2 was then bubbled through the hot solution until the tellurium precipitate was well coagulated. The solution was filtered through a sintered glass filter stick and the precipitate was discarded.

The solution remaining was evaporated to about 2 milliliters in order to drive off most of the HCl and 20 milliliters of 10 M HNO_3, 10 milligrams of Mn^{++} carrier, and 1.5 grams of $KClO_3$ were added, either by slurrying with the HNO_3 or by addition of small portions of the solid, and after the initial evolution of Cl_2 had subsided, the mixture was heated cautiously to boiling. Boiling was continued for two to three minutes to coagulate MnO_2 and the supernate was filtered off through a sintered glass filter stick. The precipitate was dissolved in 10 milliliters of 10 M HNO_3 containing two to three drops of 30% H_2O_2 and boiled for a few minutes to decompose excess H_2O_2. Ten milliliters of 10 M HNO_3 and two grams $KClO_3$ were then added and the mixture boiled for two to three minutes to reprecipitate MnO_2. The supernate was filtered off and the MnO_2 was dissolved and reprecipitated a third time by the above procedure.

The third MnO_2 precipitate was dissolved in 20 milliliters H_2O containing 0.5 milliliter 5 M HNO_3 and 2 drops of 30% H_2O_2. Ten milligrams Fe^{++} carrier was added and the solution boiled with 2 drops of saturated bromine water. 6 M NH_4OH was added dropwise until $FeOH_3$ almost precipitated, the solution was heated to boiling, and about 0.5 milliliter 3 M ammonium acetate was added dropwise to precipitate basic ferric aceate. The supernate was filtered off through a sintered glass filter stick and the precipitate dissolved in 20 milliliters H_2O containing 0.5 milliliter 6 M HNO_3. Basic ferric acetate was reprecipitated by the above procedure, filtered, and dissolved in 20 milliliters 8 M HCl. This solution was then extracted three or four times with 20 milliliter portions of isopropyl ether. The aqueous phase was then evaporated to approximately 2 milliliters to expel ether and HCl and was diluted to the desired volume.

In the process illustrated by Example II, four small scale preparations were made (less than 0.5 millicurie) and one preparation of 50 millicuries was made. In the four small scale preparations, the recovery yield ranged from 80 to 95% while in the large scale preparation the yield was 40%. This comparatively low yield was in large part due to mechanical difficulties and losses which would not ordinarily occur.

The identification of radioactive columbium values in the solutions obtained by the procedure of the above specific examples was accomplished by taking a sample of the solution, evaporating to dryness and taking an absorption curve of the sample in accordance with a standardized technique. A curve was then plotted and compared with a standard absorption curve for columbium.

In preparing a standard absorption curve for a given radioactive element, the given activity is isolated in accordance with a standardized procedure therefor. For instance, columbium activity is separated from other activities and process constituents by the precipitation of Cb_2O_5 from acid solutions. In such a method the end product is radioactive columbium in the form of Cb_2O_5 plus inactive carrier. Thus, the only measurable activity is due to the columbium.

This solution containing columbium activity as the only source of radiation is evaporated to dryness on a 1" watch glass for mounting. The evaporation is preferably accomplished by means of a radiant heater mounted above the watch glass in that heating from above causes less spattering than heating from below. Before counting, the watch glass is mounted on a stiff 3¼" x 2½" card with a 1$\frac{1}{16}$" round hole in the center. The watch glass is placed on a flat surface, a 2" x 2" thin cellophane sheet is placed over the end, the card is pressed down from above so that the watch glass, now covered with the tightly stretched cellophane, rises through the hole. A 3" x 2" strip of gummed paper or Scotch tape is then placed at the bottom of the card, sealing the watch glass into place. This method of mounting supplies firm support and good centering for the sample and prevents contamination of the counting equipment by loss of the sample.

If a beta absorption curve is to be made, the sample is placed on the third shelf on a standard Geiger-Müller counter and aluminum absorbers are placed on the second shelf. If a gamma count is to be made, the sample is placed on the third shelf of a standard Geiger-Müller counter and 1887 mg. of lead are placed on the top shelf, subsequent lead absorbers being placed at any position under the top absorber. The data for the preparation of absorption curves of the desired element is obtained by counting the sample with different thicknesses of absorbers. The data is then plotted on a standardized sheet of graph paper, thus obtaining the standard absorption curve for the given activity.

When a solution containing radioactive materials is to be analyzed, a sample thereof is mounted in accordance with the standard technique above described and the data for the absorption curves is obtained in the manner above described. The data is then plotted upon graph paper identical with that for the standard curve and the curve of the unknown activity compared with the standard curves of knwn activities. This procedure enables identification of the unknown activity.

The procedures as set forth in the above specific examples are merely illustrative of various methods of practicing our invention. Thus, the invention may be practiced without repetition of certain of the various steps as set forth therein. However, repetition of certain of the steps may be advantageous when dealing with certain types of solutions. In addition, the various reagents employed in certain phases of our process may be substituted for by other reagents, for example, potassium bromate may be utilized in the formation of the manganese dioxide in lieu of potassium chlorate as set forth above. Furthermore, the technique of complexing solutions containing columbium activity prior to separation of tellurium values therefrom may be varied considerably. For example, the oxalate for complexing may be added to the solution as such or it may be formed therein. Likewise, the basic ferric acetate employed to separate columbium activity

from the resulting manganese values may be formed externally or may be formed in the solution.

The process of our invention is of such a nature as to be readily carried out in any apparatus of suitable design and is capable of control through the necessary protective shielding employed in the handling of radioactive materials.

While our invention has been described with reference to certain specific embodiments and with reference to certain specific examples, it is to be understood that the invention is not limited thereto. Therefore, changes, additions, and/or omissions 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. In a process for the recovery of carrier-free radioactive columbium from a solution containing values of radioactive columbium and radioactive tellurium, in which said values are separated from said solution by means of an insoluble inorganic oxide carrier precipitate, the steps which comprise forming an aqueous acidic solution of said oxide precipitate and its associated columbium and tellurium values, introducing inactive tellurium in ionic form into said solution, effecting reduction of the tellurium in the resulting solution to the elemental state, separating the resulting insoluble elemental tellurium from the supernatant solution, contacting said supernatant solution with finely divided basic ferric acetate, separating the basic ferric acetate and its associated columbium values from the remaining solution, dissolving the separated basic ferric acetate and associated columbium values to form an aqueous acidic solution, and extracting the ferric ions from the resulting solution by means of an organic solvent.

2. The process of claim 1 in which the inorganic oxide carrier is manganese dioxide.

3. The process of claim 1 in which the inorganic oxide carrier is silicon dioxide.

4. The process of claim 1 in which the inorganic oxide carrier is titanium dioxide.

5. In a process for the recovery of carrier-free radioactive columbium from a solution containing values of radioactive columbium and radioactive tellurium, in which said values are separated from said solution by means of an insoluble inorganic oxide carrier precipitate, the steps which comprise forming an aqueous acidic solution of said oxide precipitate and its associated columbium and tellurium values, introducing inactive tellurium in ionic form into said solution, providing in said solution sufficient oxalate ions to complex said columbium values, effecting reduction of the tellurium in the resulting solution to the elemental state, separating the resulting insoluble elemental tellurium from the supernatant solution, contacting said supernatant solution with finely divided basic ferric acetate, separating the basic ferric acetate and its associated columbium values from the remaining solution, dissolving the separated basic ferric acetate and associated columbium values to form an aqueous acidic solution, and extracting the ferric ions from the resulting solution by means of an organic solvent.

6. The process of claim 5 in which the inorganic oxide carrier is manganese dioxide.

7. The process of claim 5 in which the inorganic oxide carrier is silicon dioxide.

8. The process of claim 5 in which the inorganic oxide carrier is titanium dioxide.

9. In a process for the recovery of carrier-free radioactive columbium from a solution containing values of radioactive columbium and radioactive tellurium, in which said values are separated from said solution by means of an insoluble inorganic oxide carrier precipitate, the steps which comprise forming an aqueous acidic solution of said oxide precipitate and its associated columbium and tellurium values, introducing inactive tellurium in ionic form into said solution, effecting reduction of the tellurium in the resulting solution to the elemental state, separating the resulting insoluble elemental tellurium from the supernatant solution, reprecipitating said inorganic oxide carrier in said supernatant solution, separating the resulting precipitate and its associated columbium values from the remaining solution, dissolving said separated precipitate and its associated columbium values to form an aqueous acidic solution, contacting the resulting solution with finely divided basic ferric acetate, separating the basic ferric acetate and its associated columbium values from the remaining solution, dissolving the separated basic ferric acetate and associated columbium values to form an aqueous acidic solution, and extracting the ferric ions from the resulting solution by means of an organic solvent.

10. The process of claim 9 in which the inorganic oxide carrier is manganese dioxide.

11. In a process for the recovery of carrier-free radioactive columbium from a solution containing values of radioactive columbium and radioactive tellurium, in which said values are separated from said solution by means of an insoluble inorganic oxide carrier precipitate, the steps which comprise forming an aqueous acidic solution of said oxide precipitate and its associated columbium and tellurium values, introducing inactive tellurium in ionic form into said solution, providing in said solution sufficient oxalate ions to complex said columbium values, effecting reduction of the tellurium in the resulting solution to the elemental state, separating the resulting insoluble elemental tellurium from the supernatant solution, reprecipitating said inorganic oxide carrier in said supernatant solution, separating the resulting precipitate and its associated columbium values from the remaining solution, dissolving said separated precipitate and its associated columbium values to form an aqueous acidic solution, contacting the resulting solution with finely divided basic ferric acetate, separating the basic ferric acetate and its associated columbium values from the remaining solution, dissolving the separated basic ferric acetate and associated columbium values to form an aqueous acidic solution, and extracting the ferric ions from the resulting solution by means of an organic solvent.

12. The process of claim 11 in which the inorganic oxide carrier is manganese dioxide.

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