NAS-NS
3013

National
Academy
of
Sciences

National Research Council

NUCLEAR SCIENCE SERIES

The Radiochemistry
of Beryllium

U.S.
Atomic
Energy
Commission

COMMITTEE ON NUCLEAR SCIENCE

L. F. CURTISS, *Chairman*
National Bureau of Standards

ROBLEY D. EVANS, *Vice Chairman*
Massachusetts Institute of Technology

J. A. DeJUREN, *Secretary*
Westinghouse Electric Corporation

H. J. CURTIS
Brookhaven National Laboratory

SAMUEL EPSTEIN
California Institute of Technology

HERBERT GOLDSTEIN
Nuclear Development Corporation of
America

H. J. GOMBERG
University of Michigan

E. D. KLEMA
Northwestern University

ROBERT L. PLATZMAN
Argonne National Laboratory

G. G. MANOV
Tracerlab, Inc.

W. WAYNE MEINKE
University of Michigan

A. H. SNELL
Oak Ridge National Laboratory

E. A. UEHLING
University of Washington

D. M. VAN PATTER
Bartol Research Foundation

LIAISON MEMBERS

PAUL C. AEBERSOLD
Atomic Energy Commission

J. HOWARD McMILLEN
National Science Foundation

W. D. URRY
U. S. Air Force

WILLIAM E. WRIGHT
Office of Naval Research

SUBCOMMITTEE ON RADIOCHEMISTRY

W. WAYNE MEINKE, *Chairman*
University of Michigan

GREGORY R. CHOPPIN
Florida State University

GEORGE A. COWAN
Los Alamos Scientific Laboratory

ARTHUR W. FAIRHALL
University of Washington

JEROME HUDIS
Brookhaven National Laboratory

EARL HYDE
University of California (Berkeley)

HAROLD KIRBY
Mound Laboratory

GEORGE LEDDICOTTE
Oak Ridge National Laboratory

JULIAN NIELSEN
Hanford Laboratories

ELLIS P. STEINBERG
Argonne National Laboratory

PETER C. STEVENSON
University of California (Livermore)

LEO YAFFE
McGill University

CONSULTANTS

NATHAN BALLOU
Naval Radiological Defense Laboratory

JAMES DeVOE
University of Michigan

WILLIAM MARLOW
National Bureau of Standards

The Radiochemistry of Beryllium

By A. W. FAIRHALL

Department of Chemistry
University of Washington
Seattle, Washington

May 1960

FOREWORD

The Subcommittee on Radiochemistry is one of a number of Subcommittees working under the Committee on Nuclear Science within the National Academy of Sciences-National Research Council. Its members represent government, industrial, and university laboratories in the areas of nuclear chemistry and analytical chemistry.

The Subcommittee has concerned itself with those areas of nuclear science which involve the chemist, such as the collection and distribution of radiochemical procedures, the establishment of specifications for radiochemically pure reagents, the problems of stockpiling uncontaminated materials, the availability of cyclotron time for service irradiations, the place of radiochemistry in the undergraduate college program, etc.

This series of monographs has grown out of the need for up-to-date compilations of radiochemical information and procedures. The Subcommittee has endeavored to present a series which will be of maximum use to the working scientist and which contains the latest available information. Each monograph collects in one volume the pertinent information required for radiochemical work with an individual element or a group of closely related elements.

An expert in the radiochemistry of the particular element has written the monograph, following a standard format developed by the Subcommittee. The Atomic Energy Commission has sponsored the printing of the series.

The Subcommittee is confident these publications will be useful not only to the radiochemist but also to the research worker in other fields such as physics, biochemistry or medicine who wishes to use radiochemical techniques to solve a specific problem.

W. Wayne Meinke, Chairman
Subcommittee on Radiochemistry

CONTENTS

The Radiochemistry of Beryllium*

A. W. FAIRHALL
Department of Chemistry
University of Washington, Seattle, Washington
May 1960

I. GENERAL REVIEWS OF THE INORGANIC AND ANALYTICAL CHEMISTRY OF BERYLLIUM

"Beryllium", pp 197-218, Vol. I. of "The Chemical Elements and Their Compounds", N. V. Sidgwick, Oxford University Press, London, 1950.

"Beryllium", pp 204-248, Vol. IV of "A Comprehensive Treatise on Inorganic and Theoretical Chemistry", J. W. Mellor, Longmans, Green and Co., London, 1923.

Gmelin's Handbuch der Anorganischen Chemie, System Nr. 26, 8th Edition, Verlag Chemie G.m.b.H., Berlin, 1930.

Chapter 32, pp 516-523, "Applied Inorganic Analysis", W. F. Hillebrand, G.E.F. Lundell, H. A. Bright and J. I. Hoffman, 2nd edition, John Wiley and Sons, Inc., New York (1953).

"Beryllium", pp 137-148, Vol. I of "Scott's Standard Methods of Chemical Analysis", N. H. Furman, editor, fifth edition, D. Van Nostrand Co., Inc., New York, 1939.

L. W. Neidrach, A. M. Mitchell and C. J. Rodden, pp 350-359, "Analytical Chemistry of the Manhattan Project", C. J. Rodden, editor-in-chief, McGraw-Hill Book Co., Inc., New York, 1950.

"Non-ferrous Metallurgical Analysis. A Review." G.W.C. Milner, Analyst 81, 619 (1956).

II. ISOTOPES OF BERYLLIUM

Only four isotopes of beryllium are known to exist, those having mass numbers 7, 8, 9 and 10. One of these, Be^8, is completely unstable, breaking up into two alpha particles in a time less than 10^{-15} sec. A short-lived isotope of mass 6 has been reported[1] but its existence is doubtful. Of the remaining three, Be^9 is the only one which is stable, and constitutes the element. Beryllium is not an abundant element, although its principal mineral, beryl, $3\ BeO \cdot Al_2O_3 \cdot 6\ SiO_2$, is rather wide spread in occurrence. The average beryllium content of rocks[2] is only about 3 ppm, and sea water[3] contains only about 5×10^{-13} g/ml of the element.

The isotopes of masses 7 and 10 are of interest in that they are both relatively long-lived nuclides. Be^7 has a half-life of close to 54 day[4], decaying by K-electron capture to stable Li^7. Of these decays, 12% go to a 0.477 Mev excited state of Li^7 and the remainder go to the ground state.[5] The only detectable radiation therefore is the 0.477 Mev γ ray, the x-rays of Li being much too soft to be detectable by present techniques. The branching ratio of 12% to the excited state of Li^7 is uncertain by 5 - 10 per cent.

Because of its rather low mass and convenient half-life, Be^7 is a nuclide of some interest in the study of nuclear reactions produced artificially in the laboratory. It arises as a spallation product[6-10] in the nuclear reactions induced at high energies, and its production at lower energies in light elements is of some interest.[11,12] Production of Be^7 by cosmic ray bombardment of the atmosphere has also been observed.[13-15]

The heaviest isotope of beryllium, Be^{10}, is quite long lived, with a half-life of 2.5×10^8y.[4] It decays by β^- emission to the ground state of stable B^{10}, and in keeping with the long half-life and consequent slow build-up to detectable intensities, the production of Be^{10} in nuclear reactions in the laboratory is not likely to be studied radio-chemically. However, Be^{10} is produced as a spallation product of cosmic ray action on the atmosphere[16,17] and on meteorites,[18] so that its occurrence in nature is of considerable interest to the geochemist.

III. REVIEW OF BERYLLIUM CHEMISTRY OF INTEREST TO RADIOCHEMISTS

1. General Considerations

In any radiochemical separation of a particular element the chemical procedures which are used are governed in part by the amount of the element which is present in the sample which is being analyzed. Isotopic carrier, in amounts of the order of milligrams, are often added to the sample to facilitate the separations and to determine the chemical recovery of the radioactive species. In the case of beryllium the amount of beryllium carrier which is to be added to the sample is governed by which of the two radioisotopes is of interest: Be^7 can tolerate relatively large amounts of carrier without interfering with the subsequent counting efficiency, whereas samples for counting Be^{10} should be as weightless as possible. Fortunately radiochemical procedures for beryllium are available which efficiently will isolate amounts of beryllium ranging from sub-microgram up to macro amounts.

In performing chemical separations with sensible quantities of beryllium present it must be born in mind that beryllium is a very toxic element. Care should be exercised to avoid ingestion of beryllium through the mouth via pipettes or by inhalation of dust or volatile beryllium compounds. If beryllium-containing solutions are spilled on the skin they should be rinsed off at once.

Beryllium is the lightest member of the group II elements. In keeping with its position in the periodic chart it has only one oxidation number, + 2. It is a very good example of the rule that the first member of a group shows a strong chemical resemblance to the second member of the next higher group: in its chemical behavior beryllium more closely resembles aluminum than it does other members of the group II elements.

Because of the electropositive nature of beryllium, and the existence of only one oxidation number for the ion, exchange between carrier and tracer species presents no problem so long as the sample containing them is completely homogeneous. The strong tendency of beryllium to hydrolyse and form colloidal aggregates above pH 5 requires that carrier-tracer exchange be carried out in fairly acid solution.

3

Many of the chemical properties of beryllium which are important in its radiochemical separations are associated with its ability to form complex ions. These complexes will be treated first.

2. Complex Ions of Beryllium

Because of its small size and its double charge, the beryllium ion has a strong tendency toward the formation of complexes. Thus the simple salts uniformly have 4 molecules of water of crystallization per beryllium atom, and the hydration of the Be^{++} ion forms a basis for understanding the strong tendency toward hydrolysis and the amphoteric properties of this species. Stability constants for several beryllium complexes are given in Table I.

The strong tendency of Be^{++} ion toward complex formation shows up in a rather peculiar way by its power to dissolve beryllium oxide. The aqueous solution of any soluble salt of beryllium can dissolve up to several molecular proportions of beryllium oxide or hydroxide. The reason for this is apparently the tendency to form the complex ion $Be(OBe)_4^{++}$, where BeO molecules have replaced H_2O molecules in the aquo complex.

Table I. Stability Constants for Beryllium Chelates

Chelating Agent	$\log K_1$	$\log K_2$	$\log K_3$	Reference
EDTA	3,5 (9.8)			2
acetylacetone	8.2	7.7		2
	9.2	7.8		48
	7.8	6.7		49
oxalic acid	4.0			2
phosphoric acid	2.54	1.8	1.4	2

The complex formed between Be^{++} and $C_2O_4^{=}$, is of some interest inasmuch as it is the only oxalate of a divalent metal which is freely soluble in water. It is a good illustration of the difference in chemical behavior of beryllium from that of the remainder of the group II

4

elements. The low degree of ionization of the compound is evidence that it exists as a chelate complex.

The complex formed between beryllium and fluoride ion is worth noting. Excess fluoride ion forms the complex anion $BeF_4^=$, which resembles very closely the sulfate anion. Thus $BaBeF_4$ forms an insoluble precipitate and finds a use in the final precipitation of beryllium in radiochemical analyses. The soluble nature of sodium fluoroberyllate can be used to advantage where mineral specimens are fused with fluorides to render them soluble.[19] The complex is a fairly strong one, but may be completely destroyed by the addition of excess H_3BO_3.

Beryllium ion is soluble in 10% $(NH_4)_2CO_3$ solution at pH 8.5-9, presumably because of the formation of a complex carbonate anion. This property of beryllium has been used in an ion exchange technique for the separation of beryllium from copper and nickel.[20]

The formation of a BeH_2PO_4 complex which limits the phosphate content of solutions which are to be used in certain cation exchange separations has been reported.[2]

3. Chelate Complexes of Beryllium

Beryllium forms numerous chelate complexes with a variety of complexing agents. These complexes may be divided into two groups according to whether they are neutral or negatively charged.

Neutral complexes are derived either from hydroxy-keto compounds, i.e. β-keto-enols, β-keto-esters and hydroxyquinones, or are a special class of covalent derivatives of carboxylic acids. A large number of hydroxy-keto compounds have been studied as chelating agents in the colorimetric determination of trace amounts of beryllium.[21] For details of these procedures the original literature should be consulted.

There are four chelating agents which deserve special mention because of the important roles which they play in radiochemical separations of beryllium. The first of these which will be mentioned is ethylenediamminetetraacetic acid (abbreviated EDTA), and for the reason that it forms a much stronger complex with many metals than it does with beryllium. Table II lists stability constants for a number of metal ions with EDTA. The value of ~ 3.8 for beryllium is sufficiently smaller than those of other common metal ions that several useful

separations may be carried out using EDTA to prevent interference from
other metal species. For example, beryllium hydroxide may be precipitated
with ammonia in the presence of aluminum, without the latter precipitating,
if excess EDTA is present. Other examples of similar applications will
be cited later.

A second very useful chelating agent for beryllium is acetylacetone.
The chelate compound beryllium acetylacetonate, $Be(C_5H_7O_2)_2$ is a low
melting (108°) volatile (b. p. 270°) solid, insoluble in water but soluble
in organic solvents. This chelate compound forms the basis for a

<div align="center">

Table II. Formation Constants of Metal - EDTA Compleces[a]

</div>

Cation	log K	Cation	log K
Vanadium (III)	25.9	Europium	17.35
Iron (III)	25.1	Samarium	17.14
Indium	24.95	Neodymium	16.61
Thorium	23.2	Zinc	16.50
Scandium	23.1	Cadmium	16.46
Mercury	21.80	Praseodymium	16.40
Gallium	20.27	Cobalt	16.31
Lutecium	19.83	Aluminum	16.13
Ytterbium	19.51	Cerium (III)	15.98
Thulium	19.32	Lanthanum	15.50
Erbium	18.85	Iron (II)	14.3
Copper	18.80	Manganese	14.04
Vanadyl	18.77	Vanadium (II)	12.70
Nickel	18.62	Calcium	10.96
Dysprosium	18.30	Hydrogen	10.22
Yttrium	18.09	Magnesium	8.69
Lead	18.04	Strontium	8.63
Terbium	17.93	Barium	7.76
Gadolinium	17.37	Beryllium	3.8

$$M^{+n} + Y^{-4} \rightleftharpoons MY^{n-4} \qquad K = \frac{MY^{(n-4)}}{M^{+n}\, Y^{-4}}$$

[a] In solutions of ionic strength 0.1. Data from reference 22, except
for Beryllium, which is from reference 2.

solvent extraction procedure for amounts of beryllium as small as the carrier-free tracer (see part III-6). Owing to the volatility of the chelate compound, care must be exercised in reducing solutions of tracer beryllium to dryness where acetylacetone has been used, in order to avoid loss of the tracer.[23]

A third chelating agent which is useful for the isolation of beryllium is the compound thenoyltrifluoroacetone (TTA). The complex with beryllium is slow to form and to decompose, a property which makes possible a solvent-extraction separation of beryllium from a number of other cations.[24] The non-volatility of this complex is an advantage over acetylacetone where tracer amounts of beryllium are concerned.

The fourth chelating agent of significance to beryllium separations is acetic acid. Beryllium is almost unique in forming a series of complex compounds with carboxylic acids, of the general formula $Be_4O (O \cdot CO \cdot R)_6$. These compounds are non-ionized, soluble in organic solvents, and volatile. The best known of these is the acetate, "basic" beryllium acetate, which is formed by treating beryllium hydroxide with acetic acid or acetic anhydride. It is generally employed for solvent extraction of beryllium in radiochemical analyses, although the stability and volatility of the complex (b.p. 330°) permits its isolation by distillation.

The second group of chelate complexes of beryllium are those which possess a negative charge. Complexes of this type have been prepared with a number of complexing anions including oxalate, malonate, citrate, salicylate and sulfate. The complex formed with oxalate has been used in the back-extraction of beryllium acetylacetone from the organic phase in a solvent extraction procedure for beryllium.[23] Complex formation with citrate has been demonstrated and used in the ion exchange separation of the group II metals.[24] The salicylate analogues sulfosalicylate and gentisic acid (2, 5-dihydroxylbenzoic acid) have been used as complexing agents in an ion exchange procedure for separation of beryllium[25] and for the spectrophotometric determination of beryllium.[26]

Details of the solvent extraction and ion exchange procedures involving chelate complexes of beryllium will be outlined in parts III-6 and -7.

7

4. Soluble Compounds of Beryllium

Beryllium hydroxide is a weak base and therefore solutions of its salts are extensively hydrolysed, forming ions like $Be(OH)^+$ and probably also colloids of the form $(BeO)_x\,Be^{++}$. Salts of such weak acids as HCN, H_2S and H_2CO_3 are almost completely hydrolysed in water. The hydrolysis of beryllium solutions leads to the absorption of beryllium onto the walls of the containing vessel. Figure 1 shows the percentage adsorption of Be^7 from carrier-free solutions in 0.1 M NaCl buffered with 0.001 M NaAc as a function of pH.[2] The pH was varied by addition of HCl or NaOH. Absorptions as high as 20% on glass containers were observed at the higher pH's.
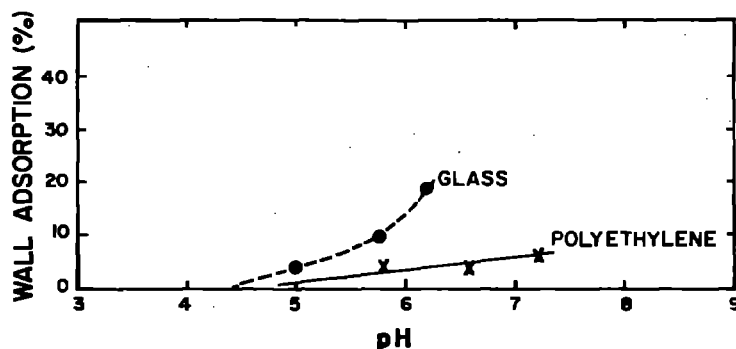

Figure 1. Adsorption of beryllium on the walls of polyethylene and glass vessels as a function of the pH of the solution. Data of reference 2.

Beryllium salts of strong mineral acids such as HNO_3, HCl, HBr, H_2SO_4, $HClO_4$, etc are all quite soluble in water and the salts themselves are usually hygroscopic. The strong tendency of beryllium to form complex ions is shown by the fact that these salts always crystallize from aqueous solution with at least 4 molecules of water per atom of beryllium, corresponding to the tetraaquo complex.

Soluble complex ions with F^-, oxalate, citrate, etc. have already been mentioned (parts III-2 and -3).

The action of strong bases such as NaOH or KOH first precipitate insoluble $Be(OH)_2 \cdot aq$, but addition of excess base causes the precipitate to redissolve. At room temperature the solubility of freshly precipitated beryllium hydroxide in 0.39 N, 0.65 N and 1.99 N NaOH is

reported to be 0.06, 0.144 and 0.66 moles of $Be(OH)_2$ per liter.[27]
The solution, however, is unstable. On long standing, or on boiling,
beryllium is reprecipitated as a dense crystalline precipitate corres-
ponding to the formula $Be(OH)_2$. The amphoteric nature of beryllium
hydroxide is a very useful property in radiochemical separations, but
whenever a strong base is used to dissolve beryllium from a mixture
of insoluble, non-amphoteric hydroxides the mixture should not be
subjected to prolonged boiling to effect solution of the beryllium lest
the opposite of the desired result be obtained.

5. Insoluble Compounds of Beryllium

The most important insoluble compound of beryllium, so far as
radiochemical separations is concerned, is the hydroxide. It is
precipitated from aqueous solution by dilute base. Because of the
amphoteric nature of the freshly precipitated hydroxide, the best
precipitant for beryllium is ammonium hydroxide buffered with NH_4^+ ion.
The precipitate of beryllium, which begins to appear at around pH 5,
is essentially insoluble in an excess of this reagent. Precipitation
of beryllium at the methyl red end point (pH ~6) has been recommended.[28]

Precipitation of dense, unhydrated $Be(OH)_2$ from boiling alkaline
solution has been mentioned above in connection with the amphoteric
properties of beryllium. A somewhat similar result is obtained if the
complex carbonate of beryllium in ammonium carbonate solution is
boiled. In this case there is obtained a white, granular precipitate of
basic beryllium carbonate of somewhat indefinite composition.
Addition of sodium bicarbonate solution to a solution of beryllium also
precipitates basic beryllium carbonate. Ignition of the hydroxides or
the basic beryllium carbonate results in beryllium oxide.

Because of the weakness of the acid, and the consequent strong
tendency to hydrolysis of the resulting compounds, the phosphates of
beryllium have a rather complicated chemistry. At lower pH's soluble
compounds may be obtained, while at higher pH's insoluble precipitates
of gelatinous nature, and therefore difficult to identify, are formed.
However, an insoluble crystalline precipitate approximating NH_4BePO_4
may be obtained by adding $(NH_4)_2HPO_4$ to beryllium solutions at pH 5.5.[29]
Ignition of the precipitate results in $Be_2P_2O_7$. This procedure is

therefore useful in obtaining beryllium in a dense form of known composition.

Another method for precipitating beryllium which has some advantages over the others involves formation of the $BeF_4^=$ complex anion by addition of excess F^- ion, followed by the addition of excess Ba^{++} ion. The solution should be acidified and only a slight excess of Ba^{++} ion should be used in order to prevent the precipitation of BaF_2. The resultant precipitate of insoluble $BaBeF_4$ is fine-grained and very difficult to filter through the usual types of dense filter paper. Digestion of the precipitate for 10 minutes prior to filtration helps somewhat, but the filtration problem can be overcome completely through the use of RA-type Millipore* filters. The compact, dense, and anhydrous precipitate does not require ignition as do the others mentioned above. This is a distinct advantage in eliminating the health hazard associated with the transfer of ignited beryllium precipitates, which tend to "dust". The $BaBeF_4$ precipitate is much more readily redissolved than ignited BeO, being easily dissolved in a mixture of H_3BO_3 and HNO_3. This is a useful property where further chemical processing is needed to remove unwanted radioactive contaminants from a beryllium sample.

Beryllium's strong tendency toward hydrolysis, and the insolubility of its hydroxide in near neutral solutions, means that beryllium will tend to co-separate on precipitates when the solution is not at least moderately acid.[29] Almost any precipitate which is formed in a solution containing beryllium at pH~7 will co-precipitate the beryllium to some extent. Particularly useful in this respect are gelatinous hydroxides such as those of aluminum and iron. Using $Fe(OH)_3$ as the co-precipitant for beryllium allows the beryllium to be recovered from the precipitate by treatment with cold NaOH solution, or by other means.

6. Solvent Extraction of Beryllium Compounds

The chelate complexes of beryllium with acetylacetone, TTA, and acetic acid, which were mentioned in part III-3 above, lend themselves

---

* Obtainable from the Millipore Filter Corporation, Watertown 72, Massachusetts.

to very useful solvent extraction procedures for beryllium. These will be given in detail below.

Acetylacetone:

By shaking or stirring aqueous solutions containing beryllium at pH 4.5 - 8 with acetylacetone a chelate complex is formed which is soluble in organic solvents. Either pure acetylacetone, a solution of acetylacetone in benzene or CCl_4 may be used. The use of a small quantity of pure acetylacetone hastens the formation of the chelate complex, after which the complex may be extracted into benzene or other suitable solvent. By stirring a solution at pH 4.5, containing about 1 microgram of beryllium with 4 ml of acetylacetone for 5 minutes, and then adding 20 ml of benzene and stirring for 20 minutes longer, Toribara and Chen found that essentially 100% of the beryllium is transferred to the organic phase.[29] Bolomey and Broido[23] shook 25 ml of 10% acetylacetone in benzene with 25 ml of a solution containing carrier-free beryllium tracer at pH 6 for 2 hours and found that all but a trace of the activity was extracted into the organic phase.

A great many other metal ions likewise form chelates with acetyl-acetone, and under the conditions described above many of them would also be extracted. The use of EDTA makes the extraction more specific for beryllium. Alimarin and Gibalo[30] studied the extraction of beryllium acetylacetonate into CCl_4, $CHCl_3$, butyl alcohol and isoamyl alcohol containing acetylacetone from aqueous solutions containing EDTA and Al, Fe, and Cr, and the divalent ions of Co, Fe, Ni, Mn, Zn, Cd, Pb, Cu, Ca and Mg. When excess EDTA was present only beryllium was extracted into the organic phase. CCl_4 proved to be the best of the solvents which were studied. In strongly ammoniacal solution aluminum and iron acetylacetonates could also be extracted.

The organic phase containing beryllium acetylacetonate may be washed with acidified water to remove unwanted impurities without the loss of appreciable amounts of beryllium[23]. About 2 drops of 0.1 N HCl to 25 ml of water makes a satisfactory wash solution for this purpose.

The beryllium acetylacetonate complex may be decomposed and the beryllium back extracted into water by shaking the organic phase

11

containing the chelate complex with equal volumes of either 10%
oxalic acid or 6 N HCl. Bolomey and Broido[23] report that 96% of
tracer beryllium is back extracted in 2 hours under these conditions.
Toribara and Chen[29] report that 15 minutes stirring of the organic
phase with 5 N HCl is sufficient to transfer the beryllium to the
aqueous phase. Because of the volatility of carrier-free beryllium
acetylacetonate, acetylacetone which dissolves in the acid used to
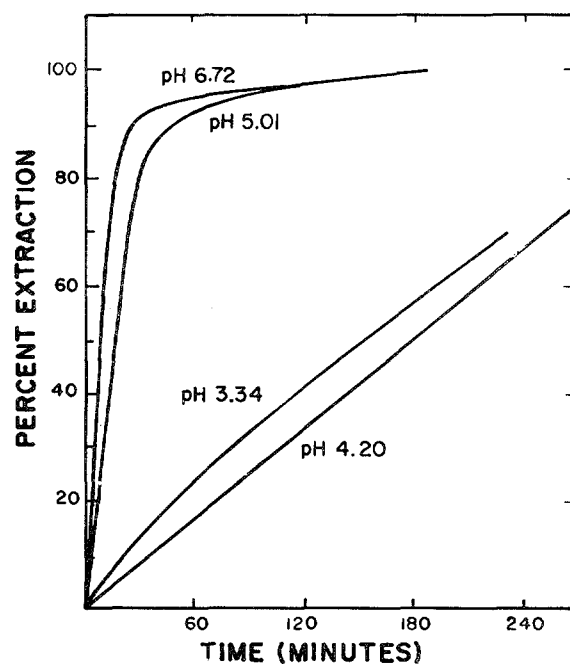
Figure 2. Rate of extraction of Be by 0.01 M TTA in benzene at
different pH values. Data of Bolomey and Wish,
reference 31.

back-extract the beryllium should be extracted from the aqueous phase
by washing the latter with one or more portions of fresh benzene. The
aqueous phase may then be evaporated to dryness under a heat lamp.
If oxalic acid is used to accomplish the back-extraction of beryllium
it may be sublimed under a heat lamp without loss of activity.[23] With
beryllium carrier present the loss of beryllium through volatilization
during evaporation of the aqueous phase does not appear to be a problem.

12

α-Thenoyltrifluoroacetetone:

Thenoyltrifluoroacetone (TTA) is a useful chelating agent for
many metals, including beryllium. Bolomey and Wish[31] have inves-
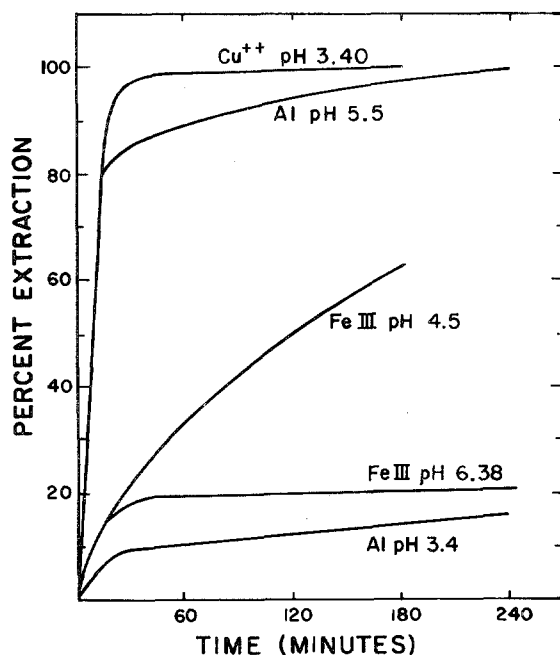
Figure 3. Rate of extraction of various metallic ions by 0.01 M TTA
in benzene at different pH values. Data of Bolomey and
Wish, reference 31.

tigated the conditions under which beryllium may be separated from
a number of other metal cations using this reagent. The complex
is rather slow to form and to decompose. In Figure 2 is shown the
rate of extraction of beryllium by 0.01 M TTA in benzene at different
pH's. The optimum pH for the extraction seems to be about 7, with
extraction of beryllium being essentially complete in about 3 hours.
The extraction of iron (III), aluminum and copper by 0.01 M TTA
in benzene at different pH values is shown in Figure 3. Evidently
aluminum is also extracted quite favorably at pH 7, but the extraction
of iron is relatively much less favorable at the higher pH.

The back-extraction of TTA complexes of Be, Al, Ca, Fe, Zn,
Sr and Y from benzene solution made 0.01 M in TTA by concentrated

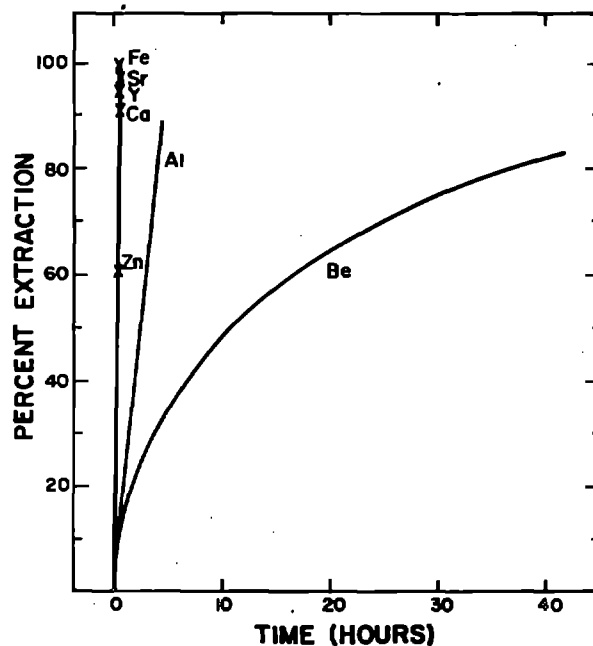Figure 4. Back extractions of several metallic ions with
concentrated hydrochloric acid. Data of Bolomey and
Wish, reference 31.

hydrochloric acid is shown in Figure 4. Back extraction of Ca, Fe,
Zn, Sr and Y is complete in 15 minutes. Aluminum requires 6 hours,
and beryllium at least 80 hours, for "complete" back-extraction.
However, the use of 2 parts concentrated formic acid to 1 part
concentrated HCl accomplishes the back-extraction of beryllium in
a matter of a few minutes (cf. Section VI, Procedure 12).

The solvent extraction method using TTA works equally well for
tracer or micro amounts of beryllium. For tracer concentrations of
beryllium TTA has the advantage over acetylacetone that there is no
loss of beryllium through volatilization of the beryllium - TTA complex.

Acetic acid.

When freshly precipitated beryllium hydroxide is evaporated slowly
to dryness several times with glacial acetic acid[32], or when beryllium
acetate is heated to $200°$ C[14], there is formed the chelate compound
$Be_4O(O \cdot CO \cdot CH_3)_6$, "basic" beryllium acetate. It is a crystalline
substance insoluble in cold water, but readily soluble in most common

organic solvents except alcohol and ether. Chloroform is the solvent most commonly employed. The solution of "basic" beryllium acetate in chloroform is remarkably stable and may be washed free of other cations by extracting with water acidified with HCl or with water alone. Recovery of beryllium from the chloroform solution may be accomplished by extraction with reagent HNO_3 or by evaporation of the chloroform followed by decomposition of the basic beryllium acetate by heating with concentrated HNO_3.

The preparation of basic beryllium acetate is somewhat time-consuming. This disadvantage is offset somewhat by the specificity of the procedure for beryllium.

7. Ion Exchange Behavior of Beryllium

The strong tendency of beryllium toward complex formation makes possible its separation by a variety of ion exchange techniques. These are summarized in Table III and discussed in detail below.

Cation Exchange Resins:

Separation of beryllium from other cation species by cation exchange may be accomplished in several ways. Beryllium is strongly absorbed on the cation exchange resin Dowex 50 at pH 6 - 8, presumably owing to colloid formation[2]. At lower pH's beryllium will pass slowly through a cation exchange resin solumn[33]. Ehmann and Kohman[28] passed a 1.1 M HCl solution containing Be and Al through a Dowex 50 column, and followed it with 1.1 M HCl. At a flow rate of 1 resin volume of eluent per 25 minutes the beryllium was completely eluted with 6 or 7 resin volumes of 1.1 M HCl. Under these conditions aluminum begins to elute only after 12 to 15 resin volumes of 1.1 M HCl have been passed through the column.

Milton and Grummitt[34] have used 1.5 M HCl as eluting agent and Dowex 50 resin to effect a separation of beryllium from the other members of the alkaline earth family. Their results are shown in Figure 5.

Honda[35] and Kakihana[36] have investigated the elution of beryllium from Dowex 50 resin by the use of dilute Ca or Mg solutions. These cations displace Be from the column, which therefore passes through,

15

but cations such as Al which are more strongly held than the alkaline earths are retained by the resin.

Complexing agents, for either unwanted cations or beryllium, have been used in the separation of beryllium by cation exchange resins. Merrill, Honda and Arnold[2] have studied the effect of various complexing

Table III. Ion Exchange Methods for the Separation of Beryllium

Cation Exchange

Resin Form	Eluting Agent	Ions Eluted	Ions Retained	Reference
HR	ca 1M HCl	Be	Al, Mg, Ca, Sr, Ba	28, 34, 35
HR	0.05 M Ca or Mg	Be		35, 36
HR	0.4 M oxalic acid	Al, Fe^{3+}, UO_2^{++} Th, others	Be	2
HR	oxalic acid pH 4.4-5	Al, Fe	Be	37
NH_4R	0.55 M Amm. lac. pH 5	Be	other alk. earths	34
NH_4R	10%$(NH_4)_2CO_3$ pH 8.5-9	Be	Cu, Ni	20
NaR	EDTA, pH 3.5-4.0	Al, Fe^{3+}, Mn^{++} heavy metals, others	Be, alk. earths	2, 38, 39
NH_4R	0.35 M acetate	Be	Al, alk. earths, U, others	2
NaR	acetylacetone pH 5	Be	Al, alk. earths U, others	2
NH_4R	0.02 M sulfosalicylic acid pH 3.5-4.5	Be	Cu, U, Ca	25

Anion Exchange

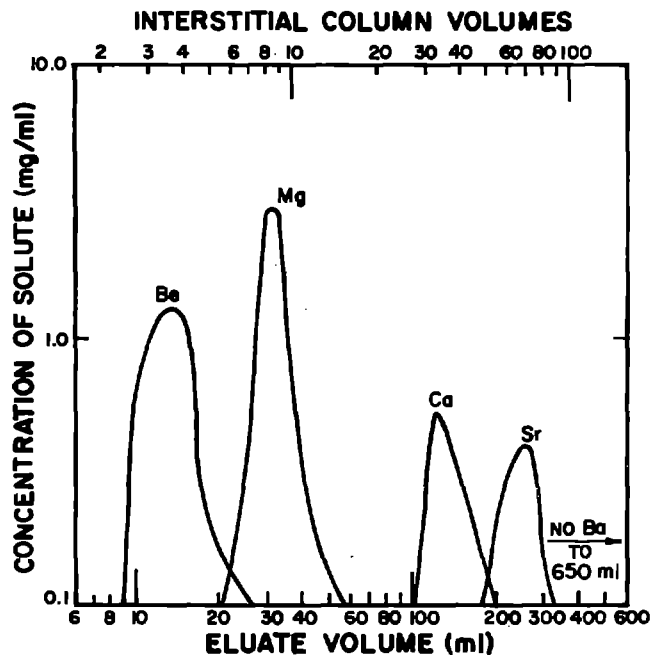|				
RC_2O_4	0.1 M oxalic acid 0.15 M HCl	Be	Al	28
RCit	1 M amm. cit. pH 8	Be	other alk. earths	24
RCl	various conc. HCl	Be	many transition elements	40-42
RCl	13 M LiCl	alk. metals, Mg	Be	43

16

INTERSTITIAL COLUMN VOLUMES

Figure 5. The separation of beryllium, magnesium, calcium,
and strontium by cation exchange using 1.5 M
hydrochloric acid eluant. Dowex 50 column 1.1
x 8 cm, flow rate 1.0 ml/min, T ~ 60° C. Data
of Milton and Grummitt, reference 34.

agents on the uptake of beryllium by Dowex 50 resin. Be^7 was used as
a tracer in these experiments which were conducted at room temperature,
23 - 25° C. They define the distribution coefficient of Be, K_d, to be

$$K_d = \frac{Be^7 \text{ adsorbed / g resin}}{Be^7 \text{ remaining / ml solution}}$$

at equilibrium. For purposes of normalization they also define the
distribution coefficient, D, to be

$$D = \frac{Be^{++} \text{ adsorbed/g resin}}{Be^7 \text{ remaining/ml solution}}$$

measured in the absence of complexing agents.

In 0.1 M Na^+, and with the resin in the sodium form, D was
measured to be 700 for 200-400 mesh resin and 830 for 50-100 mesh
resin. In 0.1 M H^+, and with the resin in the hydrogen form, D was

17

measured to be 1870 for 50-100 mesh resin. The value of D was found
to vary with the concentration, C, of the monovalent cation in the solution,
and in the neighborhood of the concentrations which were used D varied

as $\frac{1}{C^2}$. Values of the quantity $\frac{K_d}{D}$ are shown in Figure 6 plotted

against the concentration of complexing agent for several cases.

Stability constants were calculated for the several complexes from
these cation exchange data and are given in Table I, page 4.

Because certain unwanted cations may form much stronger complexes
than does beryllium, the use of complexing agents such as EDTA or
oxalate can be quite effective in isolating beryllium from a mixture of

$\frac{Kd}{D}$

$-LOG\ [A^{n-}]$

CONCENTRATION OF COMPLEXING AGENT

O = EDTA (Y^{4-}), 0.09 M Na^+–NaR $\square$ = OXALATE $(A^=)$, 0.1 M Na^+–NaR

X = ACETYLACETONE (A^-), 0.1 M Na^+–NaR   + = PHOSPHORIC ACID (A^-) 0.05 M H^+–HR

    ● = $H_2PO_4^-$ (A^-), 0.1M Na^+–NaR

◙ = OXALIC ACID $(A^=)$, 0.1 M H^+–HR

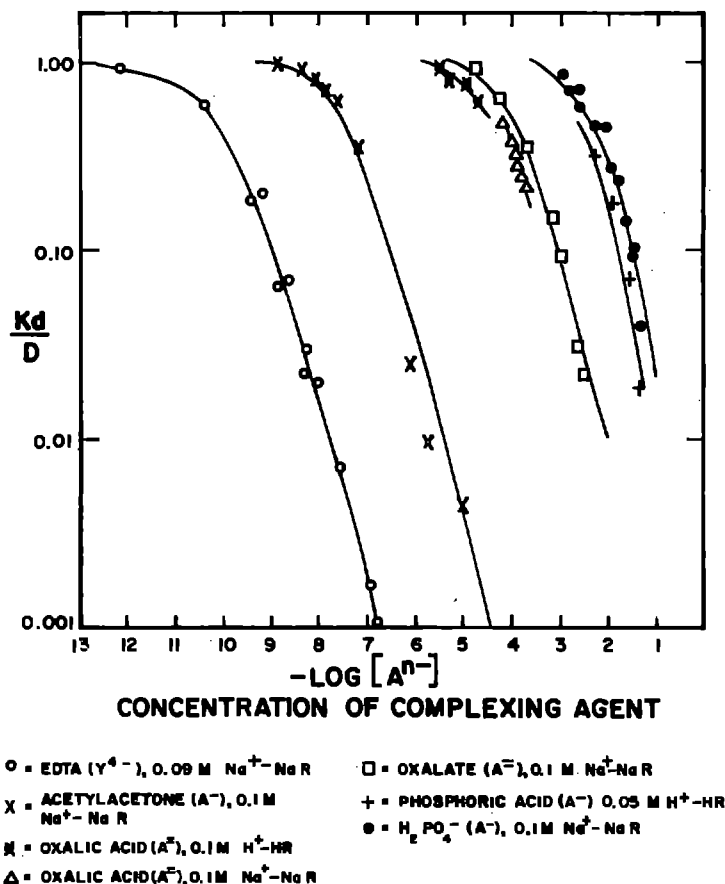△ = OXALIC ACID $(A^=)$, 0.1 M Na^+–NaR

Figure 6. Uptake of beryllium by Dowex 50 resin from
solutions containing various complexing agents.
Data of Merrill, Honda, and Arnold, reference 2.

18

cations. EDTA is especially useful in this respect, particularly in the separation of beryllium from iron and aluminum. Table IV shows the small uptake of aluminum by Dowex 50 when excess EDTA is present.[2] Using Amberlite IR-120 resin in the sodium form Nadkarni, Varde and Athavale[38] found that from solutions containing excess Na_2H_2 EDTA at pH 3.5 beryllium was absorbed by the resin while aluminum, calcium and iron passed through the column. If H_2O_2 was present titanium also passed through the column unabsorbed by the resin.

Oxalic acid is useful for the separation of beryllium from such ions as Fe^{+3}, Al^{+3}, UO_2^{+2}, and Th^{+4}. Oxalic acid, 0.4 M solution, may be used to elute these ions while beryllium is retained on the column.[2] Ryabchikov and Bukhtiarov[37] report the separation of beryllium from iron and aluminum by the use of oxalate at pH 4.4. Iron and aluminum pass through as complex ions while beryllium is retained on the column.

The separation of beryllium from magnesium and the other alkaline

Table IV. Uptake of Aluminum by Dowex 50 from Solutions
Containing Excess EDTA

Volume of solu-tion passed[a]	pH before passing	pH after passing	Al absorbed (mmole/g resin)
50	2.79	--	0.19
30	3.10	3.21	0.007
30	3.62	3.78	0.003
50	3.52	3.61	0.0026

[a] Sample solution: 0.22 M Na^+ + 0.1 M AlY^- + 0.01 M excess EDTA + $SO_4^=$; $CaCO_3$ added to adjust pH. Data of Merrill, Honda, and Arnold, reference 2.

earths by means of ammonium lactate has been described by Milton and Grummitt.[34] Using 0.55 M ammonium lactate at pH 5 as the eluant, a flow rate of 1 ml/min., and a Dowex 50 column maintained at a temperature of 78° C, beryllium was eluted from a 1.1 x 8 cm column in less than 2 interstitial column volumes. This was considerably in advance of magnesium, which began to elute at around 2.5 interstitial column volumes.

The use of salicylate analogs for selective elution of beryllium adsorbed on a Dowex 50 resin column has been reported by Schubert, Lindenbaum and Westfall.[22] Using 0.02 - 0.10 M sulfosalicylic acid at pH 3.5 - 4.5 beryllium is selectively eluted while Cu^{++}, UO_2^{++} and Ca^{++} ions remain firmly on the column. If iron is also adsorbed on the column it can be eluted before the beryllium with 0.1 M sulfosalicylic acid at pH 2.1.

When 0.1 M gentisic acid at pH 6.0 is used to elute a Dowex 50 column (H - form) containing adsorbed Ca^{++} and Be^{++} ions the beryllium comes off in a sharp band, beginning when the pH of the effluent reaches 1.9, reaching a maximum at pH 2.74 and complete when the effluent reaches pH 5.60.[25] Under these conditions calcium is still retained on the column.

Starting with 150 ml of solution containing 1.1 g of $CaCl_2$, 5 μg of Be, and 0.1 M in sulfosalicylic acid at pH 4.5, these authors passed the solution through a column containing 15 g of air-dried Dowex 50 resin which had been equilibrated with 0.1 M sulfosalicylic acid at pH 4.5. Beryllium passed completely through the column with the aid of 70 ml of wash solution (0.1 M sulfosalicylic acid at pH 4.5) while calcium was completely adsorbed.

Rapid elution of beryllium adsorbed on a cation exchange resin which has been washed free of unwanted cations may be accomplished by strong (> 3 M) HCl,[33, 38, 44] or by a solution of 0.5 M NaAc and 1 M HAc[2]. In the latter case 0.5 - 1.5 column volumes of effluent contain all the beryllium, which may be recovered as $Be(OH)_2$ by adding NH_4OH[2].

Anion Exchange Resins:

The use of anion exchange resins in the separation of metal cations implies the formation of negatively charged complex ions, either of the desired element to be separated, or of unwanted impurities. As an example of the latter, in hydrochloric acid solution beryllium does not form a complex with chloride ion of sufficient strength to be absorbed on Dowex I resin.[45] A great many other metal ions do, however, form chloride complexes which are absorbed by Dowex I resin.[40-42] Beryllium may therefore be separated from these elements by simply passing the solution in hydrochloric acid of appropriate strength

through a Dowex I resin column. Unwanted ions will be adsorbed while beryllium will pass through unadsorbed.

Even though beryllium shows negligible adsorption onto Dowex I resin from 12 M HCl solutions, it is interesting that there is adsorption of beryllium from 13 M LiCl solution.[43] With a distribution coefficient of 8 in this solution (Be adsorbed per Kg resin/Be remaining per liter of solution) beryllium could be separated by anion exchange from non-adsorbable elements such as alkali metals and magnesium by this technique.

Anion exchange separations of beryllium based on the formation of negative complexes of beryllium do not appear to have been extensively used. Ehmann and Kohman[28] have used the oxalate complex of beryllium to effect radiochemical purification of beryllium. Beryllium chloride solution, after evaporation to dryness was taken up in 0.1 M $H_2C_2O_4$ - 0.15 M HCl (pH = 0.9) solution and passed through a 4" x 1/2" column of Dowex I resin at a flow rate of 1 ml/min. Elution was by the same solution, which effected the eluution of beryllium in 5 resin volumes.

Nelson and Kraus[24] studied the separation of the alkaline earth elements by anion exchange using citrate solutions and Dowex I resin. Beryllium is more strongly absorbed than the other members of the family at low citrate concentrations, although at citrate concentrations greater than about 0.1 M magnesium is more strongly absorbed than beryllium. Effective separation of beryllium from Ca, Sr, Ba and Ra may be accomplished by this technique, but the separation from magnesium is less satisfactory. Using 1 M $(NH_4)_3$Cit at pH 8 beryllium comes off first, but the last portion of beryllium will be contaminated with magnesium. Alternatively, using 0.2 M $(NH_4)_3$Cit at pH 4.3 magnesium comes off first but tails badly and contaminates the beryllium as it is eluted from the column.

IV. PROCEDURES FOR DISSOLVING SAMPLES CONTAINING COMPOUNDS OF BERYLLIUM

Inasmuch as the common salts of beryllium, the chloride, fluoride, nitrate, sulfate etc., are freely soluble in water, the problem of

21

dissolving the sample is that of rendering soluble the matrix material in which the beryllium is imbedded. For the special case of beryllium metal itself the best solvents are hydrochloric or sulfuric acid. The metal also dissolves in alkali hydroxide solutions owing to the amphoteric character of the element. Nitric acid, either concentrated or dilute, is not a suitable solvent for it renders the metal passive.

The radioberyllium content of meteorites and of various sediments and rocks is of considerable interest to the geochemist. For iron meteorite material aqua regia is the solvent commonly employed. For siliceous materials HF is the appropriate solvent; the silica is volatilized, eliminating a bulky and otherwise troublesome component from the sample. At the same time the beryllium forms a complex with fluoride which should ensure good carrier-tracer exchange. However, care should be taken to decompose the fluorides, and the beryllium complex, before proceeding with the separation. The $BeF_4^=$ complex ion is similar in behavior to the $SO_4^=$ anion. The best method for destroying the $BeF_4^=$ complex is to treat the sample with HBO_3 after the bulk of the fluorides have been decomposed by treatment with HNO_3 or H_2SO_4.

Because of the formation of $BeF_4^=$ complex ion with fluorides, the use of a NaF fusion to render soluble the beryllium in siliceous samples has been reported by Ruml[19].

V. COUNTING TECHNIQUES FOR USE WITH ISOTOPES OF BERYLLIUM

<u>Counting of Be^7</u>

The only observable radiation from Be^7 is a γ ray of 0.477 Mev energy emitted in $\sim$ 12% of the decays (see Part II). Scintillation counting is the obvious choice for detection of these γ rays. Because of the possibility that other γ-emitting species, or β^+-emitting species which would give rise to 0.51 Mev annihilation quanta, might be present in the sample the counting of Be^7 can be done with assurance only if a γ ray spectrometer is available for examining the γ ray spectrum from the sample.

In addition to the criterion of radiochemical purity, i.e. the beryllium sample for counting must show only a 0.477 Mev γ ray,

one may also require that the sample emit no particle radiations, since Be^7 emits none. In particular, this is a requirement when Be^7 is produced in nuclear reactions in the laboratory. As discussed in Part II, production of β-emitting Be^{10} in significant intensities in these instances is negligible. For the study of Be^7 produced in nature by cosmic ray action, Be^{10} is also known to be produced[16-18] so that a low intensity of β emission from Be^{10} is to be expected.

A third criterion of the radiochemical purity of a beryllium sample is the half-life for decay of the sample, which should be 54 day. Because of the long time lapse required to establish a half-life of this magnitude, particularly for samples of low activity, it is generally desirable to establish the radiochemical purity of the sample by other means.

Where other means of establishing the identity of a radioactive species are lacking, the constancy of the specific activity (counting rate per mg of sample) of the sample when put through a number of radiochemical purification steps is usually sufficient to demonstrate that the activity is isotopic with the element of the sample.

The most difficult situation for extablishing the presence of Be^7 in a radiochemically pure condition in a counting sample arises when the intensity is very low, of the order of 30 c/m or less, in which case it may be very difficult to obtain an accurate γ ray spectrum or to detect low intensities or particle-emitting impurities. One must then fall back on the constancy of the specific activity as a criterion for establishing the identity of the activity which is being counted. One must therefore have a very reliable and specific radiochemical procedure for beryllium in order to minimize the possibility of having a radioactive contaminant in the counting sample. In this regard it is worth drawing attention to the nuclide Tl^{202}, which decays by K and L capture to Hg^{202} with the emission of 0.44 Mev γ rays. Its γ ray energy is so close to that of Be^7 that the chance of producing this species by nuclear reactions on mercury and lead isotopes should not be overlooked.

The closeness in energy of the γ ray of Be^7 to 0.51 Mev annihilation quanta makes rather easy the determination of absolute disintegration rates of Be^7 samples. Solutions of the β^+-emitting species Na^{22} which have been accurately standardized for their absolute specific

activities are commercially available for calibration purposes.
Provided the source is sufficiently thick to stop all positrons, the
rate of emission of 0.51 Mev annihilation quanta will be just twice the
positron emission rate of the source. The source may then be used to
determine the detection efficiency of the scintillation detector for
0.51 Mev quanta, which will be very close to the detection efficiency
for 0.477 Mev quanta.

Na^{22} has also a 1.28 Mev γ ray which complicates matters somewhat,
since this γ ray will also give rise to some pulses equivalent in
energy to those arising from 0.51 Mev quanta. In order to get around
this difficulty it is necessary to determine the detection efficiency of
the scintillator in the neighborhood of the 0.51 Mev photo peak. This
is best done using a scintillation spectrometer with a window which can
be opened to straddle the photopeak. Contributions to the observed
counting rate within this window from the 1.28 Mev γ ray of a Na^{22}
source may be estimated in the following way. The counting rates
in the energy region a little above and a little below the 0.51 Mev
photopeak is first measured using a rather small window to obtain the
counting rate per unit window width in these two regions. These
counting rates will be almost entirely due to 1.28 Mev quanta, and can
be used to estimate the contribution to the counting rate in the region
of the 0.51 Mev photopeak by interpolation between them. In a typical
2 inch well-type scintillation detector the contribution from 1.28 Mev
quanta to the counting rate in the 0.51 Mev photopeak amounts to about
17% of the total.

Having established the counting rate, R, of annihilation quanta which
fall within the window of the spectrometer, the detection efficienty, E,
of the spectrometer with the window straddling the 0.51 Mev photopeak
is given by

$$E = \frac{R}{2D} \cdot fa$$

D is the positron emission rate of the source and fa is a factor
to correct for absorption of 0.51 Mev quanta within the source. Provided
the source is not too thick, fa is not a very significant factor, and can
be made to cancel a similar correction factor for beryllium if the
Na^{22} sample is about the same thickness as the beryllium samples.

Having determined the counting efficiency of the scintillator for 0.51 Mev quanta, the base line of the spectrometer is shifted downward an appropriate amount so that the window of the spectrometer straddles the 0.477 Mev photopeak of Be^7. The same window width should be used as for the 0.51 Mev annihilation photopeak, in which case the detection efficiency of the spectrometer is very close to E. For a typical 2 inch well-type scintillation detector E has a value of about 6 percent for 0.5 Mev quanta.

Restricting the energy interval in which pulses will be counted to the photopeak results in an appreciable loss in counting rate of the source over that which could be obtained if a window were not used. With strong Be^7 source the disintegration rate of the source could be determined as outlined above and the sample used to determine the counting efficiency of a scintillation counter which counts all pulses above a minimum threshold. This is satisfactory for sources with counting rates in excess of a few hundred counts per minute. With very weak sources, however, counting with a window is usually to be preferred because it results in a more favorable sample-to-background counting ratio.

Counting of Be^{10}

Because of the long half life of Be^{10}, and the fact that this nuclide is likely to be of importance only in nuclear reactions produced through the action of cosmic rays, the disintegration rate of any sample containing Be^{10} will be very small indeed. When the low β decay energy of 0.555 Mev is considered also, the counting of Be^{10} becomes a formidable task. Evidently Geiger or proportional counting of thin samples in some type of low level counter is called for.

Since procedures are available for isolating beryllium in carrier-free amounts, counting samples which are very thin can be prepared. Presumably the thickness of the final sample is limited by the beryllium content of the starting material which is analysed. If such a carrier-free separation were attempted, the recovery efficiency of Be^{10} could be obtained by measuring the recovery of a Be^7 "spike" which was added at the beginning of the analysis. Of course the amount of Be^7 spike to be added should be chosen so that its counting rate does not overwhelm that due to Be^{10}. The much lower counting efficiency

of Be^7 γ radiation in a Geiger or proportional counter means that roughly 100 times the disintegration rate of Be^7 compared with Be^{10} may be present in the sample before the accuracy of counting of Be^{10} is impaired.

The identity of Be^{10} in a sample from the carrier-free separation of beryllium could be determined in a manner similar to that which is used when carrier is present. The constancy of the ratio of the Be^{10} counting rate to that of Be^7 tracer, when repeated chemical separations are performed on the sample, should suffice to demonstrate that any β activity is due to Be^{10}.

Because of the complexity of the chemical separation which may be required in some instances for isolating beryllium in a pure condition, or in high yield, it may be necessary to add beryllium carrier. In this case the final sample for counting will have an appreciable thickness, and the counting efficiency will be somewhat impaired.

Two systems for counting moderately thick Be^{10} samples have been described. The earlier of these[16] uses a thin wall cylindrical counter of the type described by Sugihara, Wolfgang and Libby.[46] The beryllium counting sample is mounted on the inside walls of two hemi-cylinders by deposition from a slurry of the sample in alcohol.

The hemicylinders are then placed in close contact with the thin wall counter. Under these conditions the geometry of the counter is about 40%. To reduce background the counter is surrounded by a ring of anti-coincidence counters. Because the sample area can be quite large under these conditions the sample can be made quite thin. However, correction for self-absorption of the radiations is necessary, and may be determined by the method of Suttle and Libby.[47]

Figure 7 shows an absorption curve in polyethylene of the radiations from Be^{10} using such a counter.[16] The measurement of the absorption curve of the radiations from a beryllium sample serves as a check on the radioactive purity of the sample, and the data may be used to calculate the self absorption of the radiations by the sample.

Ehmann and Kohman[28] have recently described a counting procedure for measuring very low levels of Be^{10} and other naturally-occurring radioactive species. They use a side-window counter having a window
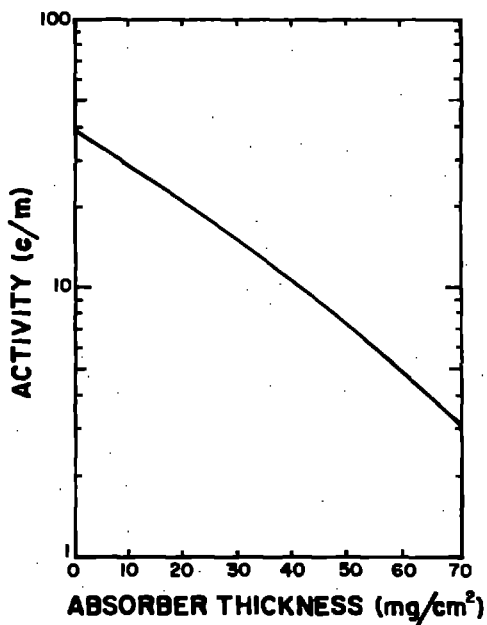
26

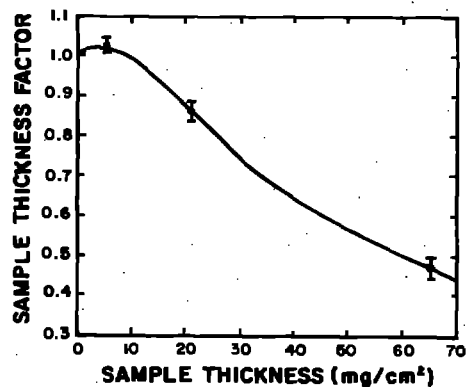Fig. 7. Absorption curve of Be[10] in polyethylene in close cylindrical geometry. Data of Arnold, reference 16.

Fig. 8. Relative counting rate per unit weight of sample for samples of Be[10] in BeO of fixed specific activity vs. the sample thicknesses. Data of Ehmann and Kohman, reference 28. The extrapolation to zero thickness was made from data of Nervik and Stevenson, reference 47.

area slightly over 6 cm^2, with a surrounding shield of anti-coincidence counters. The sample is placed in a dish close to the window of the counter in a geometry close to 40%. This system is inherently simpler to construct and operate, although counting samples will generally not be quite so thin as in the thin wall counter described above. However, self scattering in moderately thin samples helps to overcome the effects of self absorption as shown in Figure 8.

VI.   COLLECTION OF DETAILED RADIOCHEMICAL PROCEDURES
FOR BERYLLIUM

PROCEDURE 1

Separation of beryllium from stone meteorite material

Source - W. D. Ehmann and T. P. Kohman, Geochim. et Cosmochim.
          Acta 14, 340 (1958).

Procedure:

Step 1.   Rinse the specimen with acetone to remove any laquer which
           may have been used to preserve it.

Step 2.   Grind a 50-150 g sample of the specimen to a find powder
           using an electrolytic iron sheet and iron roller. Transfer
           this fine powder to a 1 liter polyethylene beaker which is
           placed in a waterbath at room temperature.

Step 3.   Dissolve the sample in a hood by the cautious addition of
           48% hydrofluoric acid. (Note 1) About 5 ml of hydrofluoric
           acid per gram of sample is used. Allow the mixture to
           stand at room temperature for 3-4 hours with occasional
           stirring.

Step 4.   Heat the mixture on a water bath at $100°$ C, with occasional
           stirring, until the mixture goes just to dryness. Add 50 ml
           of HF to the residue and again evaporate to dryness. Add
           50 ml conc. HNO_3 to oxidize iron and again reduce to dryness.

Step 5.   Dissolve the residue in 100 ml of conc. HCl and again
           evaporate to dryness to remove excess HF and HNO_3. Repeat
           the evaporation with 100 ml of conc. HCl.

Step 6.   Dissolve the residue from the evaporation in 1 l. of 9-10 M
           HCl. Filter through a funnel with fritted glass disk to remove
           insoluble residue which is usually found in trace amount.

Step 7.   Add an accurately known amount of Be carrier to the solution
           and transfer the solution to a 2 l. separatory funnel.

Extract iron with consecutive 300 - 400 ml portions of isopropyl ether which has been saturated with 9 M HCl. Three of four extractions are usually sufficient. Wash the combined ether extracts three times with 50 ml portions of 9 M HCl, combining the washings with the extracted aqueous phase.

Step 8. Reduce the volume of the solution to about 250 ml on a hot plate. To this solution add 500 ml of 12 N HCl, making the solution approximately 10 M in HCl. Pass the solution through an ion exchange column approximately 2.5 cm in diameter containing 200 - 250 ml of Dowex 1, X-10, 100 - 200 mesh ion exchange resin. Adjust the flow rate to approximately 1 ml/min. (Note 2) Wash the column with 500 ml of 10 M HCl and combine the eluates.

Step 9. Reduce the volume of the solution to 300 ml on a hot plate. Add NH_4OH to pH 7 to precipitate Al and Be hydroxides. Filter through a Millipore HA filter in a 6.5 cm Buchner funnel and wash with 25 ml of 5% NH_4Cl adjusted to pH 7.

Step 10. Dissolve the precipitate in dilute HCl and reprecipitate and filter as in Step 9. Repeat the precipitation a third time.

Step 11. Transfer the precipitated Al and Be hydroxides on the filter paper to a 250 ml beaker. Add 25 ml of 8 M NaOH and 10-20 mg of Fe (III) carrier. Macerate the filter paper and heat the mixture to boiling. Filter the warm slurry through a funnel having a 6.5 cm fritted glass disk.

Step 12. Wash the solids in the funnel with a small amount of hot water, combining the washings with the filtrate. Dilute the solution to 250 ml with distilled water and treat the solution with 6 M HCl to precipitate $Al(OH)_3$ and $Be(OH)_2$ at the methyl red end point.

Step 13. Filter off the precipitated hydroxides and redissolve them in dilute HCl. Reprecipitate the hydroxides with NH_4OH at the methyl red end point. Filter the precipitate and again repeat the precipitation at the methyl red end point.

Step 14. Dissolve the precipitated Al and Be hydroxides in the minimum amount of 6 N HCl necessary to yield complete solution. Dilute the solution to approximately 50 ml with distilled water and

adjust the acidity to 1.1 M HCl by dropwise addition of 6 M HCl, using a pH meter and standard 1.1 M HCl solution for comparison.

Step 15. Pass the solution through a 25 ml resin volume of Dowex 50, X-8, 50-100 mesh ion exchange column about 1/2 inch in diameter and 10 in. long. Adjust the flow rate to 1 ml/min. After the solution has passed through the column elution is continued with 1.1 M HCl until Be is completely eluted, usually in about 6 or 7 resin volumes. (Note 3)

Step 16. Evaporate the effluent containing Be to dryness on a steam bath. Dissolve the residue in 25 ml of 2 M HCl. Pass the solution through a 5 ml Dowex 1 ion exchange column 2 in. long and 1/2 in. in diameter. After passage of the sample solution the column is washed with 10 ml of 2 M HCl and the washing is added to the first eluate. Pb^{+2} is adsorbed in the column.

Step 17. Evaporate the eluate containing the beryllium to dryness. Dissolve the residue in 25 ml of 0.1 M $H_2C_2O_4$ - 1.5 M HCl (pH = 0.9). Pass the resulting solution through a Dowex 1 column 4 in. in length and 1/2 in. in diameter at a flow rate of 1 ml/min. Continue elution with 0.1 M H_2CO_4 - 0.15 M HCl until 5 resin volumes (about 50 ml) of the eluting solution has passed through the column. Residual Al is adsorbed on the column while beryllium passes through.

Step 18. Treat the eluate from the column with NH_4OH to pH ~ 7 to precipitate $Be(OH)_2$. Filter the precipitate on Millipore HA filter paper in a 6.5 cm Buchner funnel. Ignite the precipitate at 1000°C, weigh the BeO to determine a chemical yield, and mount the sample for counting. (Note 4)

Recycle Procedure:

Step 1. Transfer the BeO from the counting tray to a beaker and treat it with a mixture of 15 ml conc. HNO_3 and 15 ml 9 M H_2SO_4. Boil the mixture on a hot plate for 1 hour, or

until the solution is complete. Dilute the solution to 100
ml with distilled water.

Step 2. Add about 10 mg Fe (III) carrier to the solution and precipi-
tate $Fe(OH)_3$ and $Be(OH)_2$ with NH_4OH at pH ~ 7. Filter the
precipitate on Whatman No. 31 filter paper in a 6.5 cm
Buchner funnel.

Step 3. Transfer the filter paper and hydroxides to a 250 ml beaker
and treat with 15 ml of 8 M NaOH solution. Heat the solution
to boiling and filter the warm slurry through a funnel having
a 6.5 cm fritted glass disk. Wash the residue with 10 ml
of 8 M NaOH adding the washings to the filtrate.

Step 4. Dilute the combined solutions to 100 ml and add 6 M HCl
to precipitate $Be(OH)_2$ at pH ~ 7. Filter this precipitate
on Millipore HA filter paper in a 6.5 cm Buchner funnel.
Dissolve the precipitate and reprecipitate twice with NH_4OH
at pH ~ 7 to assure removal of the Na^+ present.

Step 5. Dissolve the final $Be(OH)_2$ precipitate in 25 ml of conc.
HCl and pass the solution through a 10 ml Dowex 1 anion
exchange column 4 in. long and 1/2 in. in diameter. Rinse
the column with 20 ml of conc. HCl after introduction of
the sample.

Step 6. Reduce the combined effluents from the column to 10 ml by
evaporation on a hot plate. Add 20 ml of distilled water
to make the resulting solution about 2 M in HCl. Pass
this solution through a 10 ml Dowex 1 column and rinse
the column with 20 ml of 2 M HCl.

Step 7. Combine the effluents from the column and evaporate them
to dryness. Dissolve the residue in 25 ml of 0.1 M $H_2C_2O_4$ -
0.15 M HCl and proceed as from Step 17 in the Procedure.
(Note 5).

NOTES

1. Violent effervescence is prevented by the use of the water bath for
   cooling and the slow addition of the hydrofluoric acid.

2. Residual Fe^{+3}, Co^{+2}, Cr^{+6}, U^{+4}, Pa^{+5}, Po^{+4}, Bi^{+3} and about thirty other elements are held in the column ($\log D > 1$); while Ni^{+2}, Al^{+3}, Ca^{+2}, Th^{+4}, Pb^{+2}, Ra^{+2}, and Ac^{+3} of the elements of interest pass freely through (no adsorption). The alkali elements and the other alkaline earth elements are also not absorbed.

3. Al^{+3} is held on the column, but would start to elute at about 12 to 15 resin volumes of 1.1 M HCl.

4. It is recommended that a dust mask be worn to prevent the inhalation of very toxic BeO dust.

5. The chemical procedure as given is not completely satisfactory inasmuch as the initial radioactivity usually decreases on recycling. The initial chemical yield sometimes exceeds 100 percent, indicating incomplete separation from bulk constituents, although a given specimen of stoney meteorite might contain appreciable amounts of beryllium. It appears that at least three recycles may be necessary to get rid of all contaminating activities and inert impurities. The introduction of an extraction step using acetylacetone, following the directions given in Section III-6, would probably prove of value in eliminating these difficulties. Such an extraction step could be introduced after step 13, using an excess of EDTA to hold back Al, or the extraction could be carried out following Step 17 after precipitating Be with NH_4OH.

PROCEDURE 2

Separation of beryllium from iron meteorite material

Source - W. D. Ehmann and T. P. Kohman, Geochim et Cosmochim. Acta 14, 340 (1958).

Procedure:

Step 1. Wash the sample, which may weigh from 100 to 150 g, with distilled water and acetone to remove terrestrial dirt and any lacquer which may have been used to preserve the specimen.

Step 2. Place the sample in a 2 l. beaker and treat with consecutive 200 ml portions of aqua regia. After reaction has ceased pour off each portion into a separate beaker. Continue this treatment until the specimen is completely dissolved.

Step 3. To the combined solutions add 25 ml of conc. HNO_3 to ensure oxidation of iron (II). Evaporate the solution to near dryness with several 500 ml portions of conc. HCl to remove excess HNO_3.

Step 4. To the small volume from the last evaporation add sufficient 9 M HCl to bring the volume up to 1 l. Filter the solution through a Whatman No. 50 filter paper in a Buchner funnel. A small residue, possibly graphite, may be discarded.

Step 5. Add beryllium carrier and carriers for other radioelements which it may be desired to separate. Transfer the solution to a 2 l. separatory funnel and extract iron with consecutive 300-400 ml portions of isopropyl ether saturated with 9 M HCl. Three or four extractions are usually sufficient.

Step 6. Combine the ether layers and wash them three times with 50 ml portions of 9 M HCl. Add these washings to the aqueous phase. Proceed as from Step 8 of Procedure 1 for separating beryllium from stone meteorite material. (Notes 1, 2).

NOTES

1. The chemical yield of beryllium sometimes appears to exceed 100 per cent. However, the weight of BeO often decreases appreciably on recycling, implying that the apparent extra yield comes from incomplete separation from bulk constituents rather than from beryllium present in the meteorite.

2. See Note 5 of Procedure 1.

PROCEDURE 3

Separation of beryllium from deep-sea sediments (I).

Source - P. S. Goel, D. P. Kharkar, D. Lal, N. Narsappaya, B.
Peters, and V. Yatirajam, Deep-sea Research $\underline{4}$, 202 (1957).

Core samples of ocean-bottom sediments weighed between 66 and
139 grams when dry. Beryllium was recovered from them without
addition of beryllium carrier by the following procedure. The recovery
efficienty was determined to be 80 ± 10% by spiking some sample
sediments with Be^7 tracer before the analysis.

Procedure:

Step 1.   To the dry sample add 500 ml conc. HCl and 250 ml conc.
            HNO_3. Heat to destroy organic matter and to drive off
            the acid. Destroy nitrates by repeated evaporation with
            conc. HCl.

Step 2.   Boil the semi-dry residue for 15-20 min. with conc. HCl,
            dilute with 300 ml water and heat the mixture to boiling.
            Allow the solids to settle and decant the solution. Wash
            the solid residue with 100 ml portions of 6 N HCl until
            free of iron. Combine the solutions (Solution L).

Step 3.   Boil the solid residue with 120 g NaOH in a glazed silica
            dish for 15 min and filter off any undissolved solid
            (Solution M). Fuse the solid residue with five times its
            weight of Na_2CO_3 and dissolve the melt in 100-150 ml
            of water. Filter off and discard any insoluble residue
            (Solution N).

Step 4.   Combine solutions L, M and N and heat to drive off CO_2.
            Add ammonia to pH 8 to precipitate insoluble hydroxides.
            Filter the mixture, discarding the filtrate. Dissolve the
            precipitate in 200 ml conc. HCl.

Step 5.   Evaporate the solution to dryness twice with additions of
            HCl to precipitate silica. Boil the precipitate with
            400 ml of 6 N HCl and filter (Solution O).

Step 6.   Moisten the silica residue with H_2SO_4 and heat with 48%
            HF to remove SiO_2. Fume any remaining residue with H_2SO_4,
            ignite it and then fuse it with Na_2CO_3. Dissolve the melt

34

in HCl and filter. Combine the filtrate with Solution O.

Step 7. Add ammonia to Solution O to bring the pH to 8. Filter the precipitated hydroxides and discard the filtrate. Dissolve the precipitate in 500 ml 6 N HCl.

Step 8. Extract Fe(III) from the solution by shaking with 1 liter of ether. Concentrate the aqueous phase to 150 ml, add 15 g NH_4Cl and cool in an ice bath. Add 300 ml of ether and pass in HCl gas. Filter off the precipitate of Al and Ti chlorides. Evaporate the filtrate to 50 ml volume.

Step 9. Add 8 g disodium EDTA to the solution and adjust the pH to 4.5-5.0 by the addition of dilute NH_4OH. Add 2.5 ml acetylacetone and shake for 5 minutes.

Step 10. Extract beryllium from solution with four 100 ml portions of benzene, shaking the mixture for 10 minutes each time. Combine the benzene layers and back-extract beryllium by shaking with four 175 ml portions of 6 N HCl.

Step 11. Combine the HCl extracts and evaporate the solution to dryness. Destroy any organic matter by evaporation with aqua regia. Take up the residue from the evaporation in about 40 ml of 1 N HCl.

Step 12. Cool the solution in an ice bath and add 10 ml of 6% cupferron solution. Extract the mixture with three 40-ml portions of $CHCl_3$, and discard the organic phase. Evaporate the aqueous phase to dryness and decompose organic matter by evaporation with HNO_3.

Step 13. Decompose residual nitrates by boiling the residue with HCl. Evaporate the solution to dryness and take up the residue in 5 ml of dilute HCl. Transfer the solution a little at a time to a plastic counting dish and evaporate to dryness under a heat lamp.

PROCEDURE 4

Separation of beryllium from deep-sea sediments (II).

Source - P. S. Goel, D. P. Kharkar, D. Lal, N. Narsappaya, B.
Peters, and V. Yatirajam, Deep-sea Research $\underline{4}$, 202 (1957).

A simplified procedure for recovering Be^{10} from samples of ocean-
bottom sediments, assuming that the beryllium is adsorbed on the
surface of the clay particles.

Procedure:

Step 1.   Add 5 mg of BeO to the dried sample and heat the sample to
500°C in a muffle furnace for 2 hours to destroy organic
matter.

Step 2.   Leach the ignited material 4 times with 190 ml of conc. HCl
and then wash the insoluble residue with 1:1 HCl solution
until the washings are colorless.

Step 3.   Combine the acid leach and washings and evaporate the
solution to small volume. (Note 1) Take up the residue
in water and add 400 g of disodium EDTA. Adjust the
pH of the solution to 4.5 - 5.

Step 4.   Add 5 ml acetylacetone and shake for 5 minutes. Then
extract the solution with four portions of benzene, shaking
the mixture for 10 minutes each time.

Step 5.   Wash the combined benzene extracts with water at pH 5.
Discard the washings and back extract beryllium with
four portions of 6 N HCl.

Step 6.   Transfer the solution a little at a time to a plastic counting
dish and evaporate to dryness under a heat lamp. (Note 2)

NOTES

1. The procedure as quoted in the original article states that an
   acetylacetone-benzene extraction is carried out directly on the
   HCl solution after the disodium EDTA has been added. Since the
   extraction with acetylacetone must be carried out from solutions
   of pH greater than 4.5, the considerable quantity of base which
   would be needed to bring the strongly acid solution to the proper

pH would result in a very large volume of solution to be extracted. The details of the procedure from this point onward are not given in the original article. Steps 3, 4 and 5 represent an attempt at giving specific details of the procedure based upon information given in the original article.

2. It remains to be demonstrated to what extent this simplified procedure is capable of recovering Be^{10} from samples of sedimentary material.

PROCEDURE 5

Separation of beryllium from Clay by a solvent extraction procedure.
Source - J. R. Merrill, M. Honda, and J. R. Arnold,
(to be published).

Procedure:

Step 1. Divide the clay sample into ca. 100 g units. Disperse each of them in a small amount of water in a 1 liter, heat-resistant polyethylene beaker. To the mixture slowly add 250 g of 48% HF followed by 80 ml of concentrated H_2SO_4. Add about 10 mg of beryllium carrier to the mixture.

Step 2. Transfer the mixture to a 300 ml platinum dish and heat very slowly over a small gas flame. Continue heating until the viscous solution which remains begins to solidify. Cool the mixture.

Step 3. Heat the residue with 300 ml of water. Centrifuge any undissolved material, which should consist mainly of black organic matter and aluminum and calcium sulfates (Note 1). If much unattacked original sample is present further bisulfate treatment is necessary. Combine the supernatant solutions from the several clay units (Note 2).

Step 4. To the combined solutions add EDTA in about 20% excess over the amount estimated for complexing the Fe and Al present. Add sufficient water to bring the volume of the solution to about 3 liters.

Step 5. Adjust the pH with ammonia to about 6.4 (Note 3). When the solution becomes cool again add 25 ml of acetylacetone and stir until it is dissolved. Transfer the solution to a large separatory funnel and extract the beryllium complex with three 250 ml portions of benzene (Note 4).

Step 6. Combine the benzene extracts and wash them with 500 ml of water buffered to pH 5-6 with dilute acetate. Discard the aqueous layer. Back-extract beryllium from the benzene solution with two 150 ml portions of 6 M HCl.

Step 7. Combine the HCl extracts and add 45 g of disodium EDTA and enough ammonia to bring the pH to 6.4. Allow the solution to cool, then add 10 ml of acetylacetone and stir until it is dissolved. Transfer the solution to a separatory funnel and extract with three 100 ml portions of benzene.

Step 8. Combine the benzene extracts, and after washing with 200 ml of buffered water, back-extract beryllium with two 50 ml portions of 6 N HCl. Combine the HCl extracts in a large beaker, add 10 ml of conc. HNO_3 and heat the solution (caution!). Boil the solution nearly to dryness with repeated additions of HNO_3.

Step 9. Take up the residue from the evaporation in water and add ammonia to bring the pH to 8. Filter the precipitated $Be(OH)_2$ and ignite to BeO.

Step 10. Weigh the BeO to determine chemical yield and mount for counting (Note 5).

NOTES

1. In a preliminary experiment, a Stockton shale sample was used as a model and Be^7 tracer was used to measure the recovery of beryllium. With about 10 mg of beryllium carrier it was found that the hot water extracts of the sulfate cake contain almost all of the beryllium whereas 70-80% of total aluminum was left in solid form.

2. Sometimes the brown supernatant solution contains some suspension (aluminum compound).

3. The color of the iron - EDTA complex is useful as an indicator.

4. Occasional difficulties of separation require centrifuging the organic layer at this step.

5. The over-all yield of beryllium is about 60-70%. The procedure has been sufficient to remove all radioactive impurities from the clay samples which were analysed, but beryllium carrier is necessary for good results.

PROCEDURE 6

Separation of beryllium from clay by an ion exchange procedure.

Source - J. R. Merrill, M. Honda, and J. R. Arnold, (to be published).

Procedure:

Steps 1-3   As in Procedure 5, using 20 mg of BeO carrier for a 200-300 g clay sample.

Step 4.   Take 0.5 ml of the combined aqueous extracts of the sulfate cake and analyse by EDTA complexiometric titration for Fe and Al (Note 1).

Step 5.   Add gradually a mixture of $2 H_4Y + 1 Na_2H_2Y \cdot 2 H_2O + 5 CaCO_3$ to the solution until about 0.1 mole of excess EDTA, over that needed to complex Fe and Al, has been added. Adjust the pH to 3.5-4 with more $CaCO_3$ (usually about 100 g). (Note 2).

Step 6.   Add 60 ml of glacial acetic acid as a buffer (Note 3). Filter off the insoluble $CaSO_4$ - $CaCO_3$ and dilute the filtrate and washings to 10 liters.

Step 7.   Pass the solution through a 1 liter Dowex 50 x 8 ion exchange column in the sodium form. After this solution has passed through, pass through 1 liter of 0.01 M EDTA + 0.1 M NaAc + 0.5 M HAc to remove any traces of Al and Mn adsorbed on the column. (Note 4).

Step 8.   Elute beryllium from the column with a solution of 0.5 M NaAc and 1 M HAc. About 0.5-1.5 column volumes of effluent contain all the beryllium.

Step 9.   Precipitate $Be(OH)_2$ from the effluent by the addition of
ammonia. Filter the precipitate and ignite to BeO. Weigh
to determine chemical yield and mount for counting.

NOTES

1. For discussions of complexometric titration see G. Schwarzenbach,
Analyst 80, 713 (1955); "die Komplexometrische Titration", G.
Schwarzenbach, F. Enke, Stuttgart (1955); "Complexometric
Titrations", G. Schwarzenbach and H. Irving, Methuen and Co. Ltd.,
London, Interscience Publishers, Inc., New York. (1957).

2. Calcium carbonate is used to raise the pH so that the electro-
lyte concentration will not be increased. Beryllium is not
coprecipitated with $CaSO_4$.

3. If appreciable amounts of Mg or Ca are in solution they will
replace Na^+ from the ion exchange resin used in the succeeding
step. In the presence of excess EDTA this increases the pH of
the solution, the most important variable in the process. To prevent
this enough HAc is added to the mixture to make the final solution
0.1 M.

4. The completeness of removal can be checked by complexometric
titration of the effluent.

PROCEDURE 7

Separation of beryllium from clay

Source - J. R. Arnold, Science 124, 584 (1956).

Procedure:

Step 1.   The sample, consisting of several hundred grams of wet
clay, is treated with a mixture of 500 g of 48% HF and
500 g of 12 N HCl in two 1 liter HH polythene beakers, after
10 ml of Be carrier (approximately 60 mg BeO equivalent)
has been added. Evaporate to dryness in a hot-air jet.

Step 2.   Add 150 g of each acid and again evaporate to dryness.
            Evaporate to dryness twice more with a total of 500 g
            of HCl to remove most of the fluoride.

Step 3.   Take up the sample in 1500 ml of 1 N HCl, boil, decant, and
            centrifuge. Heat the remaining solid with H_2SO_4 until
            HF bubbles cease.

Step 4.   Take up the cake with water and fuse any remaining solid
            with $KHSO_4$. After dissolving the melt in water, discard
            any solid which remains and combine all solutions.

Step 5.   Add 650 g of tetrasodium EDTA and bring the solution to
            pH 6 to 6.5. Add 25 ml of acetylacetone, and after the
            solution has stood for 5 minutes extract with three 250-ml
            portions of reagent-grade benzene. Combine the benzene
            extracts and backwash them with acetate-buffered water at
            pH 5.5 to 6.

Step 6.   Extract the benzene layer with two 150 ml portions of 6 N
            HCl and discard the organic phase. Add 45 g of disodium
            EDTA to the aqueous extracts and adjust the pH to 6 to 6.5.
            Add 10 ml of acetylacetone, and after the solution has
            stood extract it with three 75 ml portions of benzene.

Step 7.   Combine the benzene extracts, backwash them with acetate-
            buffered water at pH 5.5 to 6, and then back-extract with
            two 50-ml portions of 6 N HCl. Discard the organic phase.

Step 8.   Boil down the aqueous phase nearly to dryness with the addition
            of HNO_3 to destroy organic matter. Take up in 50 ml of
            water and precipitate $Be(OH)_2$ with ammonia. Filter the
            precipitate and ignite to BeO.

Step 9.   Weigh the BeO to determine chemical recovery and mount
            for counting.

PROCEDURE 8

Separation of beryllium from aluminum target material.

Source - E. Baker, G. Friedlander, and J. Hudis, Phys. Rev. 112, 1319 (1958).

Bombarded aluminum targets contain Na^{22}, which gives 0.51 Mev quanta that interfere with the counting of the 0.48 Mev γ ray of Be.

Procedure:

Step 1.   Dissolve the aluminum in acid and add beryllium carrier.

Step 2.   Precipitate beryllium and aluminum hydroxides with ammonia. Centrifuge and discard the aqueous phase.

Step 3.   Dissolve the mixed hydroxides in concentrated hydrochloric acid, add an equal volume of ether to the solution, cool in an ice bath, and saturate the solution with HCl gas. Centrifuge and discard the precipitate of $AlCl_3 \cdot 6\,H_2O$.

Step 4.   Evaporate the liquid phase to small volume on a steam bath. Add distilled water and precipitate $Be(OH)_2$ with ammonia. Centrifuge and discard the aqueous phase.

Step 5.   Dissolve the precipitate of $Be(OH)_2$ in glacial acetic acid and transfer the solution to a casserole. Evaporate to dryness on a steam bath. Repeat the evaporation to dryness with glacial acetic acid three more times.

Step 6.   Take up the solid, consisting of crystals of basic beryllium acetate, in $CHCl_3$ and transfer the $CHCl_3$ solution to a separatory funnel. Wash the $CHCl_3$ layer three times with an equal volume of water. Discard the aqueous layer.

Step 7.   Evaporate the $CHCl_3$ layer to near dryness. Take up the residue in a small amount of HNO_3. Again take the solution to dryness and them dilute with water. Precipitate $Be(OH)_2$ by adding a slight excess of HN_4OH.

Step 8.   Filter the $Be(OH)_2$ precipitate through a Whatman No. 42 filter paper. Transfer to a platinum crucible, char the paper, and ignite at 1000° for 1 hour. Grind the BeO to a powder, slurry with 5 ml of ethanol and filter onto a weighed filter paper disc. Dry in an oven and weigh to determine chemical yield. Mount for counting.

PROCEDURE 9

Separation of beryllium from mixed fission products and uranium.

Source - J. D. Buchanan, J. Inorg. Nuc. Chem. 7, 140 (1958).

Essentially the same procedure has been described by Baker, Friedlander, and Hudis, Phys. Rev. 112, 1319 (1958) for the separation of beryllium from cyclotron targets of copper, silver and gold. Two cycles of the procedure have resulted in a decontamination factor of 3×10^8 and a chemical yield of 90%.

Procedure:

Step 1.   Dissolve the sample in an appropriate acid and add beryllium (about 15 mg) to the sample contained in a centrifuge tube (50 ml). Stir well, then precipitate $Be(OH)_2$ with a slight excess of NH_4OH. Centrifuge and discard the supernatant solution.

Step 2.   Dissolve the $Be(OH)_2$ precipitate in 10 ml conc. HCl. Pass through a short column of Dowex 1X-10 resin which has been washed with conc. HCl (Note 1). Wash the resin with 5 ml conc. HCl. Collect the effluent in a centrifuge tube.

Step 3.   Reprecipitate $Be(OH)_2$ with a slight excess of NH_4OH. Centrifuge and discard the supernatant solution. Wash the precipitate with 15 ml of water and discard the wash.

Step 4.   Dissolve the $Be(OH)_2$ precipitate in min. of conc. HCl. Add 3 mg Fe III carrier, dilute to 15 ml and heat on a water bath. Add 10 ml 8 N NaOH with stirring, and heat until $Fe(OH)_3$ coagulates. Centrifuge and decant the supernatant solution to a clean centrifuge tube.

Step 5.   Acidify the solution with HCl and then precipitate $Be(OH)_2$ with a slight excess of NH_4OH. Centrifuge and discard the supernatant solution.

Step 6.   Dissolve the precipitate in 3 ml glacial acetic acid and dilute the solution to 15 ml with water. Add 2 ml of 10% EDTA solution and then adjust the pH to 5 with NH_4OH using indicator paper.

Step 7.   Add 2 ml of acetylacetone and stir the solution vigorously for a minute with a mechanical stirrer. Add 7 ml of benzene

and extract beryllium by stirring vigorously for a minute with the mechanical stirrer. Allow the two phases to separate and transfer the benzene phase to a clean centrifuge tube by means of a transfer pipette. Check the pH of the aqueous phase and readjust to pH 5 if necessary.

Step 8. Repeat step 7 twice more, combining the benzene extracts with that from step 7.

Step 9. Back extract beryllium by adding 10 ml of 6 N HCl to the benzene solution and stirring vigorously for 1 min. Allow the phases to separate and transfer the HCl solution to a 150 ml beaker using a transfer pipette.

Step 10. Repeat step 9 once, combining the HCl extract with the first in the 150 ml beaker. Discard the benzene layer.

Step 11. Evaporate the HCl solution just to dryness (do not bake). Add 5 ml of conc. HNO_3 and evaporate just to dryness. (Note 2).

Step 12. Dissolve the residue from step 11 in 2 ml of conc. HNO_3 and 10 ml of water. Add a slight excess of NH_4OH to precipitate $Be(OH)_2$. Filter with suction on Whatman No. 42 paper. Transfer the paper and precipitate to a crucible and dry under a heat lamp or in a 100° oven. Ignite the precipitate to BeO at 1000°C for 1 hr or until precipitate is snow white.

Step 13. With the crucible inside a hood to avoid inhaling BeO dust, grind the BeO to a powder with a stirring rod. Transfer the BeO to a tared filter paper by slurrying with alcohol. Wash with ethanol and dry at 90-100° for 10 min. Weigh the sample as quickly as possible as BeO is somewhat hygroscopic. Mount BeO for counting.

NOTES

1. The ion exchange column is made by sealing a tip 5 mm long by 2 mm diameter to the bottom of a 15 x 85 mm pyrex test tube, plugging the tip with glass wool, and filling the tube with resin to a height of about 1 inch.

2. If a higher degree of decontamination is needed, dissolve the
   residue in 10 ml conc. HCl and repeat the procedure from step 2.

PROCEDURE 10

Separation of beryllium from cyclotron targets

Source - J. B. Ball, G. H. Bouchard, Jr., A. W. Fairhall, and
      G. Mitra (unpublished).

The following procedure is used where the target meterial is
sandwiched between silver foils and bombarded with up to 44 Mev helium
ions. Be^7 which escapes from the target is caught in the silver foil.
No Be^7 is produced under these conditions in the silver foil itself. Because
of activation of impurities in the silver foil several hold-back carriers
are used to improve the decontamination of the beryllium. The procedure
is sufficiently general that a large number of target elements could be
handled without much modification. The over-all chemical yield is
in excess of 80%.

Procedure:

Step 1.   Dissolve the target and silver catcher foils in conc. HNO_3.
           Evaporate most of the excess acid and add Be carrier
           (10 mg). Add hold-back carriers of Cu, Zn, Cd, In, Au,
           Hg and Tl, where possible as nitrates (Note 1).

Step 2.   Dilute the mixture to about 20 ml with water and pass in
           H_2S until the precipitated sulfides are well coagulated.
           Centrifuge the mixture and decant the supernatant solution
           to a clean centrifuge tube. Discard the precipitate.

Step 3.   Add conc. NH_4OH to the solution until the solution is
           faintly ammoniacal. Centrifuge the mixed precipitate of
           $Be(OH)_2$ and sulfides and discard the aqueous phase.

Step 4.   Add 6 N NaOH in sufficient amount (about 1 ml) to dissolve
           the $Be(OH)_2$ from the precipitate. Dilute the mixture to
           about 20 ml with water. Centrifuge and discard any
           precipitate which may be present.

Step 5.   To the supernatant solution add 3 to 4 drops of 10 mg/ml
           Fe III carrier, with swirling. Centrifuge and discard the
           precipitated $Fe(OH)_3$.

Step 6.   Add a drop or two of methyl red indicator and barely acidify
           the solution. Then add sufficient NH_4OH to turn the indicator
           yellow. Centrifuge the precipitate of $Be(OH)_2$.

Step 7.   Dissolve the $Be(OH)_2$ precipitate in a small amount of
           conc. HCl. Dilute the solution to 20 ml with water and
           add 2 ml of a saturated solution of the disodium salt of
           EDTA. Precipitate beryllium with NH_4OH. Centrifuge and
           discard the supernatant solution. Repeat the precipitation
           of $Be(OH)_2$ in the presence of EDTA twice more.

Step 8.   Dissolve the $Be(OH)_2$ precipitate in a minimum of conc.
           HCl. Dilute to 20 ml with water, transfer the solution
           to a 50 ml plastic centrifuge tube and add 30 drops conc.
           HF. Heat the solution in a boiling water bath and
           slowly precipitate $BaBeF_4$ by dropwise addition of 5 ml
           of a saturated solution of $Ba(NO_3)_2$. Continue heating
           for 10 minutes and then centrifuge the precipitate.
           Before discarding the supernatant solution check for
           completeness of precipitation by adding 1 drop more each
           of Ba solution and conc. HF.

Step 9.   Take the precipitate up in a small amount of distilled
           water and filter the suspension through a weighed RA-type
           millipore filter (Note 2). Wash with distilled water
           and dry in an oven. Weigh as $BaBeF_4$. Mount for counting.

NOTES

1. Gold carrier necessarily contains chloride ion which precipitates
   AgCl. A small amount of AgCl precipitate in the mixture makes
   no difference to the recovery of beryllium.

2. The precipitate is very fine-grained and next to impossible to
   filter through ordinary filter paper.

Radiochemical separation of beryllium

Source - T. T. Shull, in "Collected Radiochemical Procedures",

Los Alamos Scientific Laboratory Report La-1721, 2nd ed. (1958)

1. Introduction

The determination of radioberyllium (Be^7) is based upon the formation, after the appropriate decontamination steps, of basic beryllium acetate, $Be_4O(OCOCH_3)_6$, which is extractable by chloroform. The first decontamination step carried out on a solution of the sample is a ferric hydroxide precipitation by means of an excess of sodium hydroxide solution. Beryllium, as a result of its amphoteric nature, remains in solution as a beryllate, $NaHBeO_2$ or Na_2BeO_2. The beryllate is then converted to beryllium ion and beryllium hydroxide precipitated with ammonia water. The hydroxide is purified by a series of acid sulfide precipitations in the presence of molybdenum, antimony, and tellurium carriers, respectively. Beryllium hydroxide is then changed to the basic acetate by acetic acid treatment. The basic acetate is extracted into chloroform, the chloroform is evaporated, and the basic acetate is dissolved in nitric acid solution. Beryllium is finally converted to the oxide, BeO, in which form it is weighed and counted. The procedure as outlined below requires approximately 18 hours and gives chemical yields in the neighborhood of 35%. Although decontamination factors have not been determined, it appears that decontamination from gamma-emitting impurities is of a very high order.

2. Reagents

Be carrier: 1.082 mg Be/ml (3.00 mg BeO/ml)--(added as c.p. $BeSO_4 \cdot 4H_2O$ in H_2O)

Fe carrier: 10 mg Fe/ml (added as $FeCl_3 \cdot 6H_2O$ in dilute HCl)

Mo carrier: 10 mg Mo/ml (added as $NH_4)_6Mo_7O_{24} \cdot 4H_2O$ in H_2O)

Sb carrier: 10 mg Sb/ml (added as $SbCl_5$ in $2\underline{M}$ HCl)

Te carrier: 10 mg Te/ml (added as $TeCl_4$ in dilute HCl)

HCl: 6 $\underline{M}$

HCl: conc.

HNO_3: conc.

$HC_2H_3O_2$: glacial

NH_4OH: conc.

NaOH: 20% by weight aqueous solution

H_2S: gas

Chloroform: anhydrous

Ethanol: absolute.

3. Equipment

Fisher burner

Drying oven

Muffle furnace

Centrifuge

Block for holding centrifuge tubes

Mounting plates

Forceps

Tongs for Erlenmeyer flasks

10-ml beakers (one per sample)

50-ml beakers (two per sample)

Pipets: 1- and 10-ml

125-ml separatory funnels (two per sample)

125-ml Erlenmeyer flasks (one per sample)

Ground-off Hirsch funnels: Coors 000A (one per sample)

Filter chimneys (one per sample)

Filter flasks (one per sample)

No. 42 Whatman filter circles: 7/8" diameter--washed with ethanol,
   dried, and weighed

No. 42 Whatman filter paper (9 cm)

2", 60° filter funnels (four per sample)

40-ml conical centrifuge tubes: Pyrex 8320 (14 per sample)

Wash bottle

Steam bath

Hot plate

Stirring rods.

4. Preparation of Standard Beryllium Carrier

Dissolve 10.62 gm of c.p. $BeSO_4 \cdot 4H_2O$ (Brush Beryllium Co.),
which has been dried overnight at 105°, in 500 ml of H_2O. This gives a
solution containing 1.082 mg Be/ml (equivalent to 3.00 mg BeO/ml).

5. Procedure

Step 1. Pipet exactly 10 ml of standard Be carrier into a 40-ml
conical centrifuge tube and add an aliquot of the sample and
1 ml of conc. HCl. Heat to boiling and add 0.5 ml of Fe
carrier. Bring the solution nearly to neutral by the dropwise
addition of 20% NaOH. Transfer the solution to another
40-ml centrifuge tube which contains sufficient 20% NaOH
to give the combined solution a 5% NaOH concentration. Stir
vigorously during the transfer. Heat on a steam bath for
5 min, centrifuge, transfer the supernate to a clean centrifuge
tube, and retain the $Fe(OH)_3$ precipitate for Step 4.

Step 2. Add 0.5 ml of Fe carrier to the supernate with constant,
vigorous stirring. Centrifuge, transfer the supernate to a
clean centrifuge tube, and retain the $Fe(OH)_3$ precipitate for
Step 4.

Step 3. Neutralize the supernate by the dropwise addition of conc. HCl.
Make the solution ammoniacal with conc. NH_4OH. Heat for
5 min on a steam bath and then let the mixture stand for at
least 10 min, proceeding in the meantime with Step 4.

Step 4. Combine the $Fe(OH)_3$ precipitates from Steps 1 and 2. Dissolve
the combined precipitate in a minimum of conc. HCl. Transfer
the solution into another centrifuge tube containing sufficient
20% NaOH solution to give to the combined solution a 5%
NaOH concentration. Heat on a steam bath for 5 min.
Centrifuge and transfer the supernate to a clean centrifuge
tube, discarding the precipitate (Note 1). Neutralize the
supernate with conc. HCl and then make it ammoniacal with
conc. NH_4OH. Heat on a steam bath for 10 min.

Step 5.   Centrifuge the $Be(OH)_2$ precipitates formed in Steps 3 and 4. Combine both supernates in a 125-ml Erlenmeyer flask (Note 2). Combine both precipitates by washing the smaller into the larger. Stir to break up the precipitate and then centrifuge. Transfer the wash liquor to the 125-ml flask above.

Step 6.   Dissolve the $Be(OH)_2$ precipitate in a slight excess of conc. HCl and repeat Steps 1-5.

Step 7.   Dissolve the $Be(OH)_2$ precipitate in a minimum of 6 $\underline{M}$ HCl, add an additional milliliter of 6 $\underline{M}$ HCl, and dilute to 10 ml with H_2O. Add 0.5 ml of Mo carrier and bubble in H_2S for 5 min. Centrifuge and decant the supernate into a clean centrifuge tube, discarding the precipitate. Heat the supernate for 10 min on a steam bath, pass in H_2S for 2 to 3 min, and dilute to 20 ml with H_2O. Centrifuge, transfer the supernate to the clean centrifuge tube and discard the precipitate.

Step 8.   Heat the supernate to expel H_2S. Add 0.5 ml of Sb carrier and saturate with H_2S. Centrifuge and decant the supernate into a clean centrifuge tube, discarding the precipitate.

Step 9.   Heat the supernate to expel H_2S and add 0.5 ml of Te (IV) carrier. Boil and saturate with H_2S, centrifuge, and filter through a No. 42 Whatman filter paper using a 2", 60° funnel into another centrifuge tube (Note 3).

Step 10.   Heat the filtrate to expel H_2S and then make ammoniacal with conc. NH_4OH. Centrifuge and discard the supernate. Acidify the $Be(OH)_2$ precipitate with 5 ml of glacial $HC_2H_3O_2$ and evaporate the solution nearly to dryness, with constant stirring over a low flame. Add 5 ml of glacial $HC_2H_3O_2$ and evaporate to dryness over a flame, being careful not to let the temperature exceed 330°, the boiling point of basic beryllium acetate. Let the tube cool to room temperature and extract the basic beryllium acetate with $CHCl_3$, using one 10- and three 5-ml portions of $CHCl_3$ and centrifuging each time before decanting the supernate into a 125-ml separatory funnel. Retain the solid material in the centrifuge tube.

Wash the $CHCl_3$ extract four times with 4-ml portions of H_2O, transferring the wash liquor to the centrifuge tube containing the material which was not extracted by $CHCl_3$. Filter the $CHCl_3$ solution through <u>dry</u> No. 42 Whatman filter paper into a clean, dry 50-ml beaker, using a 2", 60° filter funnel. Evaporate the $CHCl_3$ on a steam bath. While the $CHCl_3$ is being evaporated, proceed with Step 11.

Step 11.   Acidify the wash liquor and the $CHCl_3$-insoluble material from Step 10 with conc. HCl. Precipitate $Be(OH)_2$ by the addition of conc. NH_4OH. Centrifuge. If an appreciable quantity of $Be(OH)_2$ is formed, convert it to the basic acetate as in Step 10 and repeat the $CHCl_3$ extraction, adding the basic acetate extracted to that obtained in Step 10.

Step 12.   Dissolve the basic acetate from the evaporated $CHCl_3$ extract by heating with a minimum of conc. HNO_3. If it is felt that sufficient decontamination has been obtained, proceed immediately to Step 14. However, it is necessary ordinarily to proceed as in Step 13.

Step 13.   Transfer the solution to a clean centrifuge tube. Dilute the HNO_3 solution to 15 ml with H_2O and precipitate $Be(OH)_2$ by the addition of conc. NH_4OH. Centrifuge and discard the supernate. Repeat Steps 7-12.

Step 14.   Evaporate the HNO_3 solution to 1 to 2 ml and transfer to a 10-ml beaker. <u>Carefully</u> continue heating (on a hot plate) to dryness. Ignite for 1 hour at 250° in a muffle furnace. Cool, slurry the BeO with 3 to 5 ml of absolute ethanol, and pour onto a tared No. 42 Whatman filter circle in a filter chimney-ground-off Hirsch funnel set up which contains 10 ml of absolute ethanol. Permit the solid to settle evenly on the filter circle (this requires about 10 min) before applying suction. Dry the precipitate by pulling air through the funnel for 2 to 5 min; then dry at 105° for 15 min. Cool and weigh. Mount and gamma-count in scintillation counter (Note 4). Be^7 has only a 476-kev gamma ray.

NOTES

1. An additional recovery of Be from the $Fe(OH)_3$ precipitated in Step 4 increases the chemical yield by about only 1 to 2%.

2. The supernates from the $Be(OH)_2$ precipitations in Steps 3 and 4 are saved as a precautionary measure. If much $Be(OH)_2$ appears to have been lost at this stage, these supernates can be evaporated to a small volume and made ammoniacal for further recovery of Be. A small quantity of $Be(OH)_2$ is always formed by this treatment.

3. Steps 8 and 9 probably could be combined with Step 7, i.e., all three carriers, Mo, Sb, and Te, could be added at the same time and precipitated as sulfides.

4. Counting is begun immediately and is continued at intervals for a period of at least 53 days (one half-life of Be^7). It is well to check immediately for the presence of beta activity to determine whether any impurity which is both a beta and a gamma emitter is contaminating the Be^7 and must be corrected for.

Addendum to Beryllium Procedure

1. If an appreciable amount of iron remains with the beryllium, i.e., enough to impart a yellow color to the $Be(OH)_2$ precipitate, just prior to the basic acetate step, it is advisable to make an ether extraction from 6 $\underline{M}$ HCl before proceeding.

2. The solids from the acetic acid evaporation are heated to a temperature of approximately 220° C to complete the formation of basic beryllium acetate. About 30% of the Be is converted to the basic acetate at 118 to 120°; however, 95 to 97% is converted at 220° C. Care must be exercised to prevent the temperature from exceeding 330° and thus decomposing the basic acetate already formed. The final heating is best accomplished in a constant temperature oil bath or under a heat lamp.

3. The final, BeO, after ignition at 500° is transferred directly to an aluminum counting plate rather than being slurried with alcohol and filtered. More reproducible results are obtained in this manner.

Separation of Beryllium from Fission Product Mixtures

Source - G. M. Iddings, in "Radiochemical Procedures in Use at the
University of California Radiation Laboratory (Livermore)",
University of California Radiation Laboratory Report UCRL-4377
(1954).

Purification: From a 4-day old solution containing 10^{14} fissions and
about 10^9 beta counts per minute, a sample of Be^7 was
obtained which showed a beta activity of about 7 c/m.

Yield: About 70 per cent

Separation time: About six hours exclusive of ignition.

Step 1.　　To an acid solution of mixed activities, add 10 mg Be carrier
and about 5 mg of lanthanum carrier.

Step 2.　　Make the solution ammoniacal. Centrifuge and wash
precipitate with dilute ammonia. Discard supernatant and
wash.

Step 3.　　Add 10 ml 3 $\underline{N}$ NaOH to the precipitate. Digest for not more
than five minutes in a not water bath. Centrifuge. Repeat
leach with another 10 ml 3 $\underline{N}$ NaOH. Combine NaOH
supernatants. Discard residual $La(OH)_3$.

Step 4.　　Add ~ 5 mg Te^{+4} carrier to the NaOH solution. Add 5 drops
of a saturated solution of Na_2S. Add ~ 15 ml of a saturated
solution of NH_4Cl. Centrifuge and wash $Be(OH)_2$ precipitate
twice with water. Discard supernatants.

Step 5.　　Dissolve $Be(OH)_2$ in 3 or 4 drops of conc. HCl, and add
~ 15 ml of a buffer solution of 0.5 $\underline{N}$ Na_2SO_3 and 1 $\underline{N}$ $NaHSO_3$
(~pH 6).

Step 6.　　Transfer solution to a 60-ml, cylindrical, open-top,
separatory funnel (with stem detached immediately below the
stopcock).

Step 7.　　Add 30 ml of 0.40 $\underline{M}$ TTA (thenoyltrifluoracetone) in benzene
and equilibrate phases for ten minutes by rapid stirring with
a motor-driven glass rod stirrer (paddle).

Step 8.   Wash organic phase twice with ~ 15 ml of water allowing
three minutes for each wash (to remove the sulfite). Wash
organic phase twice with ~ 15 ml of 8 $\underline{N}$ HNO_3 for five
minutes each wash (see Note 1).

Step 9.   Wash organic phase six times with ~ 12 ml of a solution whose
composition is ~ 11 $\underline{N}$ HCl and 1 $\underline{M}$ H_2SO_4 (11 ml conc.
HCl with 0.7 ml conc. H_2SO_4) allowing ten minutes for
each wash (see Note 2).

Step 10.   Add ~ 15 ml of a solution consisting of two parts conc.
formic acid and 1 part conc. HCl. Agitate layers together
for 15 minutes. Repeat and combine aqueous layers.

Step 11.   Make solution ammoniacal. Centrifuge the precipitate and
wash with water.

Step 12.   Add 10 ml of 3 $\underline{N}$ NaOH and add Br_2 dropwise until solution
becomes yellow. Stir. Add a saturated solution of Na_2S
dropwise until solution becomes colorless, then add 5 drops
excess (to keep any Te in solution when the pH is lowered
to 9 or 10 in the next step).

Step 13.   Add 10 ml of a saturated solution of NH_4Cl. Centrifuge
precipitate and wash with water.

Step 14.   Acidify with HCl to pH 3-4 (by adding ~ 20 ml of 0.1 $\underline{N}$ HCl).
Add ~ 5 mg Fe^{+++} carrier. Warm to ~ 60°C in water bath.

Step 15.   Add 1.5 ml of 5% 8-quinolinol in 2 $\underline{N}$ HAc. Add 5-10 ml of
2 $\underline{N}$ NH_4Ac to bring solution to ~ pH 5. Let stand for five
minutes in 60°C bath, then cool to room temperature.
Filter through No. 42 Whatman paper. Discard precipitate.
(Separation of Be from Al, Pa, Zr, Nb and others.)

Step 16.   Make filtrate basic with NH_4OH. Filter through No. 42
Whatman paper. Wash with 1% solution of NH_4Ac.

Step 17.   Ignite to BeO for one hour at 1000°C.

Step 18.   Transfer to tared aluminum hat and weigh rapidly   (BeO
is somewhat hygroscopic.) Add a few drops of Zapon
(diluted fourfold with ethyl acetate).

PROCEDURE 12 (CONTINUED)

NOTES

1. Te^{+4} is slowly reduced to Te metal by the sulfite, and it is carried along at the interface of the benzene-aqueous mixture. A 5-minute wash with 8 $\underline{N}$ HNO_3 will oxidize finely divided Te metal to Te^{+4}, placing it in the acid layer. The paddle stirrer is necessary to churn the two phases together very rapidly.

2. 10 or 12 $\underline{N}$ HCl will bring Np^{+4} from 0.4 $\underline{M}$ TTA into the aqueous phase. 12 $\underline{N}$ HCl with some sulfate will cause Zr, and some of Pa, to be extracted into the aqueous phase.

3. If very large amounts of protactinium are present initially, extra steps must be added to remove this activity.

REFERENCES

1. H. Tyren and P. A. Tove, Phys. Rev. $\underline{96}$, 773 (1954).

2. J. R. Merrill, M. Honda, and J. R. Arnold, to be published. The author is grateful to Dr. Arnold for a copy of their manuscript in advance of its publication.

3. J. R. Merrill, E. F. X. Lyden, M. Honda, and J. R. Arnold, Geochim. et Cosmochim. Acta (in press).

4. References to original literature may be found in "Tables of Isotopes", D. Strominger, J. M. Hollander, and G. T. Seaborg, Revs. Mod. Phys. $\underline{30}$, No. 2, Part II, April 1958.

5. See F. Ajzenberg and T. Lauritsen, Revs. Mod Phys. $\underline{27}$, 77 (1955), p 87.

6. L. Marquez and I. Perlman, Phys. Rev. $\underline{81}$, 953 (1951).

7. J. M. Dickson and T. C. Randle, Proc. Phys. Soc. (London) $\underline{64A}$, 902 (1951).

8. G. Friedlander, J. M. Miller, R. Wolfgang, J. Hudis, and E. Baker, Phys. Rev. $\underline{94}$, (1954).

9. G. Friedlander, J. Hudis, and R. L. Wolfgang, Phys. Rev. $\underline{99}$, 263 (1955)

10. E. Baker, G. Friedlander, and J. Hudis, Phys. Rev. $\underline{112}$, 1319 (1958).

11. H. D. Holmgren and R. L. Johnston, Phys. Rev. $\underline{113}$, 1556 (1959).

12. G. H. Bouchard, Jr. and A. W. Fairhall, Phys. Rev. $\underline{116}$, 160 (1959).

13. J. R. Arnold and H. A. Al-Salih, Science $\underline{121}$, 451 (1955).

14. A. J. Cruikshank, G. Cowper, and W. E. Grummitt, Can. J. Chem. $\underline{34}$, 214 (1956).

15. K. Siegbahn, A. Berggren, and B. Ingelman, Arkiv f. Fysik 11, 445 (1957).

16. J. R. Arnold, Science 124, 584 (1956).

17. P. S. Goel, D. P. Kharkar, D. Lal, N. Narsappaya, B. Peters, and V. Yatirajam, Deep-sea Research 4, 202 (1957).

18. W. D. Ehmann and T. P. Kohman, Geochim. et Cosmochim. Acta 14, 364 (1958).

19. V. Ruml, Chem. Prumysl 5, 480 (1955); C. A. 50, 7652c (1956).

20. T. A. Belyavskaya and V. I. Fadeeva, C. A. 51, 11162h (1957).

21. See for example reference 2 (above); Adam, Booth, and Strickland, Anal, Chim. Acta 6, 462 (1952); Cucci, Neuman, and Mulryan, Anal. Chem. 21, 1358 (1949); Kosel and Neuman, ibid 22, 936 (1950); Underwood and Neuman, ibid 21, 1348 (1949); Meek and Banks, ibid 22, 1512 (1950); Sill and Willis, ibid 31, 598 (1959); Karanovich, Zhur. Anal. Khim 11, 400 (1956).

22. G. Schwartzenbach, R. Gut, and G. Anderegg, Helv. Chim. Acta 37, 937 (1954).

23. R. A. Bolomey and A. Broido, Atomic Energy Commission Report ORNL-196 (1948).

24. F. A. Nelson and K. A. Kraus, J.A.C.S. 77, 801 (1955).

25. J. Schubert, A. Lindenbaum, and W. Westfall, Chimia 11, 50 (1957); J. Phys. Chem. 62, 390 (1958).

26. H. V. Meeks and C. V. Banks, Anal. Chem. 22, 1512 (1950).

27. J. Rubenbauer, Zeit. anorg. Chem. 30, 334 (1902).

28. W. D. Ehmann and T. P. Kohman, Geochim. et Cosmochim. Acta 14, 340 (1958).

29. T. Y. Toribara and P. S. Chen, Jr., Anal. Chem. 24, 539 (1952).

30. I. P. Alimarin and I. M. Gibalo, Zhur. Anal. Khim. 11, 389 (1956).

31. R. A. Bolomey and L. Wish, J.A.C.S. 72, 4483 (1950).

32. G. Urbain and H. Lacombe, C. R. 133, 874 (1901).

33. R. M. Diamond, J.A.C.S. 77, 2978 (1954).

34. G. M. Milton and W. E. Grummitt, Can. J. Chem. 35, 541 (1957).

35. M. Honda, J. Chem. Soc. Japan 71, 118 (1950); ibid 72, 361 (1951).

36. H. Kakihana, *ibid.* 72, 203 (1951).

37. D. I. Ryabchikov and V. E. Bukhtiarov, Zhur. Anal. Khim. 9, 196 (1954).

38. M. N. Nadkarni, M. S. Varde, and V. T. Athavale, Anal. Chim. Acta 16, 421 (1957).

39. T. Taketatsu, J. Chem. Soc. Japan 79, 586 (1958); *ibid* 79, 590 (1958).

40. G. E. Moore and K. A. Kraus, J.A.C.S. 74, 843 (1952).

41. K. A. Kraus and G. E. Moore, *ibid.* 75, 1460 (1953).

42. K. A. Kraus and F. Nelson, Proc. Int. Conf. on Peaceful Uses of Atomic Energy, Geneva 1955, Paper 837, Vol. 7, 113 (1956).

43. K. A. Kraus, F. Nelson, F. B. Clough and R. C. Carlston, J.A.C.S. 77, 1391 (1955).

44. T. Y. Toribara and R. E. Sherman, Anal. Chem. 25, 1594 (1953).

45. K. A. Kraus, F. Nelson, and G. W. Smith, J. Phys. Chem. 58, 11 (1954).

46. T. T. Sugihara, R. L. Wolfgang, and W. F. Libby, Rev. Sci. Inst. 24, 511 (1953).

47. W. E. Nervik and P. C. Stevenson, Nucleonics 10, No. 3, 18 (1952).

48. B. E. Bryant, J. Phys. Chem. 58, 573 (1954).

49. R. M. Izatt, W. C. Fernelius, and B. P. Block, J. Phys. Chem. 59, 80 (1955).