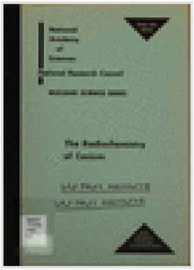

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The Radiochemistry of Cesium

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Upton, New York

February 1961

Subcommittee on Radiochemistry
National Academy of Sciences—National Research Council

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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, 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

INTRODUCTION

This volume which deals with the radiochemistry of cesium is one of a series of monographs on radiochemistry of the elements. There is included a review of the nuclear and chemical features of particular interest to the radiochemist, a discussion of problems of dissolution of a sample and counting techniques, and finally, a collection of radiochemical procedures for the element as found in the literature.

The series of monographs will cover all elements for which radiochemical procedures are pertinent. Plans include revision of the monograph periodically as new techniques and procedures warrant. The reader is therefore encouraged to call to the attention of the author any published or unpublished material on the radiochemistry of cesium which might be included in a revised version of the monograph.

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II. TABLE OF ISOTOPES OF CESIUM(68,84)

Isotope	$T_{1/2}$	Type of Decay	Energy of Decay Particles Mev (relative intensities)	Formation
Cs^{123}	6 m	β^+		
Cs^{125}	45 m	β^+ E. C.	β^+ 2.05 γ 0.112	$I^{127}(\alpha,6n)$
Cs^{126}	1.6 m	β^+ 82% E. C. 18%	β^+ 3.8 γ 0.385	Daughter Ba^{126}
Cs^{127}	6.25 h	β^+ E. C. $\frac{\text{E. C.}}{\beta^+} \rightarrow$ 15	β^+ 0.68, 1.06 γ 0.125(10),0.286(?) 0.406(80),0.440(weak)	Daughter Ba^{127} $I^{127}(\alpha,4n)$
Cs^{128}	3.8 m	β^+ 75% E. C. 25%	β^+ 1.5(3),2.5(30),3.0(70) γ 0.445,0.980	Daughter Ba^{128}
Cs^{129}	31 h	E. C. no β	γ 0.04(460)*,0.092(11.4)*, 0.174(0.35)*,0.283(1.36)*, 0.315(~1.2)*,0.371(13.2)*, 0.411(~10)*,0.545(0.52)*, 0.585(~0.22)* *relative Ce_k intensities	Daughter Ba^{129} $I^{127}(\alpha,2n)$
Cs^{130}	30 m	β^+ 46% E. C. 52% β^- 1.6%	β^+ 1.97(28) β^- 0.442(1)	$I^{127}(\alpha,n)$

II. TABLE OF ISOTOPES OF CESIUM (Continued)

Isotope	$T_{1/2}$	Type of Decay	Energy of Decay Particles Mev (relative intensities)	Formation
Cs^{131}	9.9 d	E. C. no β^+		Daughter Ba^{131} Ba^{130}(n,γe) I^{127}(α,γ)
Cs^{132}	6.2 d	E. C. ~98%	γ 0.670(100),1.08(0.6),1.20(0.6),1.30(1)	Cs^{133}(n,2n) Cs^{133}(25-Mev p,pn)
Cs^{133}	Stable	100% abundance		
Cs^{134m}	3.1 h	IT 99% β^- ~ 1%	β^- ~0.55 γ 0.0105(98%),0.127(98%),0.137(0.8%)	Cs^{133}(n,γ) Cs^{133}(d,p)
Cs^{134}	2.2 y	β^-	β^- 0.083(32%),0.31(5%),0.665(50%),0.683(13%), γ 0.473(1.8),0.563(9),0.569(13),0.605(100),0.795(91),0.801(18),1.038(0.9),1.168(3.0),1.367(4.6)	Cs^{133}(n,γ) Cs^{133}(d,p) Ba^{136}(d,α)
Cs^{135}	2.0x10^{6} y	β^-	β^- 0.21	Daughter Xe^{135} U(n,f)
Cs^{136}	12.9 d	β^-	β^- 0.341(92.6%) 0.657(7.4%) γ 0.0672,0.153,0.162,0.265,0.335,0.882,1.04,1.245,1.41,2.35,2.49	La^{139}(n,α) U(n,f)

Cs^{137}	30	y	β^-	β^- γ	0.514(92.4%) 1.18(7.6%) 0.662(with Ba^{137m})	Daughter Xe^{137} U(n,f)
Cs^{138}	32	m	β^-	β^- γ	3.40 0.139(2.0%),0.193(0.8%), 0.229(1.6%),0.411(3%), 0.463(23%),0.550(8%), 0.87(4%),1.01(25%), 1.43(73%),2.21(18%), 2.63(9%),3.34(0.5%)	Descendant I^{138} Daughter Xe^{138} Ba^{138}(n,p) U(n,f)
Cs^{139}	9.5	m	β^-	β^-	4.3	Daughter Xe^{139} Descendant I^{139} U(n,f)
Cs^{140}	66	s	β^-			Daughter Xe^{140} U(n,f)
Cs^{141}	short		β^-			Daughter Xe^{141}
Cs^{142}	~1	m	β^-			U(n,f)
Cs^{143}	short		β^-			Daughter Xe^{143}
Cs^{144}	short		β^-			Daughter Xe^{144}

III. Review of those Features of Cesium Chemistry of Interest to Radiochemists

GENERAL PROPERTIES

Cesium is a member of the homologeous series NH_4-K-Rb-Cs the members of which show greater similarity in their properties and those of their compounds than the members of any other group with the possible exception of the halogens. The element is widely distributed in nature almost always associated with the other alkalis and usually in small amounts. The highest concentration of cesium occurs in pollucite (34% Cs_2O) which generally contains little or no rubidium. Cesium is obtained from the carnallites of the Stassfurt region which contain only small percentages of cesium and rubidium, but these are concentrated in the large scale extraction of potassium.

CESIUM METAL

The metal is silvery white in the pure state but is frequently a golden yellow due to the presence of small amounts of oxide or nitride. Cesium is the most active and the most electro-positive of all the metals, and on exposure to air it tarnishes quickly and melts due to the formation of impurities or bursts into flame. It has the largest atomic volume of any metal. The reaction between cesium and moisture cannot be detected at temperatures below -116°C; this may be compared with -108°C for rubidium, -105°C for potassium, and -98°C for sodium. Metallic cesium is of greatest interest for the manufacture of photoelectric cells; it possesses the greatest advantage that its range of sensitivities corresponds closely to that of the human eye. The properties of the metal are summarized in Table I.

The metal was first prepared by Setterberg in 1881, by the electrolysis of a mixture of CsCN and $Ba(CN)_2$. The action of magnesium or rare earth metals in the form of "Mischmetal" is particularly suitable for the preparation of metal from

Table I

Atomic and Physical Properties of Cesium(Cs)

Atomic weight		132.91
Atomic number		55
Melting point, °C		28.4
Boiling point, °C		690
Density, 20°C		1.90
Nucleus [Neutrons		78
[Protons(+)		55
Electrons in various quantum levels:	1st	2
	2nd	8
	3rd	18
	4th	18
	5th	8
	6th	1
Ionizing potentials of gaseous atoms, volts		3.87
Potential required to remove electrons from solid metal		-
Potential between metal and normal aqueous solution of ion; $M = M_{aq} + e^{-}$		3.02
Heat of hydration of gaseous ions, kcal		63
Ionic radius in crystals, cm x 10^{8}		1.69

cesium oxide. The metal has also been prepared from Cs_2CO_3 by heating with magnesium; or by heating CsCl with calcium chips in a stream of dry hydrogen. Colloidal solutions of cesium have been prepared in ether by arcing two noble metal electrodes; aerosols have also been formed in gases. The colloidal cesium is bluish green, closely resembling the color of the vapor.

HALIDES

Cesium chloride can be obtained by prolonged recrystallization of carnallite, which contains the slightly soluble cesium alum. A preferred preparation consists of precipitation with silicomolybdic acid, followed by treatment with gaseous HCl to volatilize molybdenum and fractional crystallization from alcohol to separate the other chlorides. The bromides and iodides are made from the hydroxide by treatment with free halogen; this yields mixtures of iodate-iodide and bromate-bromide, respectively. The mixtures are evaporated and the bromate and iodate are reduced, e.g., by heating with carbon or in a stream of H_2S.

Cesium halides are body centered cubic with the exception of CsF which is face centered; the sides of the cubes are as follows (A°):

CsF	6.01 (face centered)
CsCl	4.12
CsBr	4.29
CsI	4.56

In contrast to the other alkali halides the solubility of cesium halides decreases from chloride to iodide; the properties of the halides are summarized in Table II.

Table II

Properties	CsF	CsCl	CsBr	CsI
Melting point, °C	683	626	627	621
Boiling point, °C	1250	1303	1300	1280
Heat of vaporization, kcal		39.750	36.870	44.820
Heat of dissociation, kcal/mole $(MX — M^{+}_{gas} + X^{-}_{gas})$		98.9	99.0	100
Interionic distances (x 10^{8}cm)				
Measured, A		3.06	3.14	3.41
Calculated, A		3.07	3.18	3.43
Critical temperature (calc.),°C		2421	2433	2407
Solubility, g/100 g H_2O				
0°C	366.5 (18°)	161.4	123 (25°)	44
100°C		270.5		160 (61°)
Heat of formation,kcal/mole		106.32	97.65	83.90

Polyhalides

Cesium, because of its large atomic volume, easily forms polyiodides which are very stable and fairly insoluble. The cesium polyiodides, CsI_3 and CsI_4, can be formed by simply evaporating a solution of iodine in CsI. The analogous bromine salts are also known, but not the chlorides. There are, however, a considerable number of mixed polyhalides; e.g., $CsIBr_2$, $CsICl_2$, $CsBrCl_2$, $CsClBr_2$. These all crystallize readily from aqueous solutions of their components and range in color from the black of the polyiodides through "dichromate-orange" to the pale yellow of the brom-chloride. Their stability is considerable, CsI_3

reaching a decomposition pressure of 1 atmosphere only at 250°C. Another halide, $CsICl_4$, is also known and may be considered as the addition compound of the chloride with iodine trichloride. It can be formed in various ways from the aqueous solutions of the components, e.g., from the chloride and iodine chloride, from the iodate and chlorine, or from iodate and hydrochloric acid. It exists as fine yellow needles which, upon exposure to air, give off iodine trichloride.

Complex Halides

Cesium also forms complex halides which are frequently difficultly soluble compounds and which may be used in the detection or estimation of the accompanying metal. Examples of such compounds are: Cs_3SbCl_5; $4CsCl \cdot 4SbCl_3 \cdot FeCl_3$; red $Cs_2Bi_2I_9$; yellow $Cs_2NaCo(NO_2)_6$ capable of detecting 0.01 mg of Co; Cs_3InCl_6, transparent octahedral crystals capable of detecting 0.02 g of In; $Cs_2PbCu(NO_2)_6$, employed to detect Pb or Cu and a corresponding nickel compound used to detect Ni; $Cs_9Bi_5Na_6(NO_2)_{30}$, a bright yellow compound capable of detecting 0.02 mg of $NaNO_2$ in the presence of Tl, Zn, Cd, alkaline earths, or other alkali metals; Cs_2TeCl_6, lemon yellow, sensitive test for Te, applicable in the presence of Se; Cs_2SnCl_4, white crystals; Cs_2PtCl_6, yellow; $Cs_2CuHgCl_6$; $CsAuCl_4$; $CsAg_2Au_2Cl_{12}$; $Cs_4ZnAu_2Cl_{12}$; $Cs_2Mg_2Fe_2(CN)_{12}$.

Perchlorate

The general properties of perchlorates depend to a large extent on the large volume and symmetrical structure of the perchlorate ion. Perchlorates of metals with large atomic volumes (K, Rb, and Cs) are not greatly hydrated; consequently, cesium perchlorate, $CsClO_4$, is somewhat insoluble (1.6 g in 100 g of water at 20°C). The solubility is considerably reduced in ethanol solution at 0°C.

The perchlorate is prepared by evaporation of an appropriate salt with perchloric acid, by heating the chlorate, e.g.,

$$4CsClO_3 \longrightarrow CsCl + 3CsClO_4$$

and by anodic oxidation of weakly acidic chloride solution. The latter technique yields first the chlorate and then the perchlorate; low temperature, high emf, and high current density favor the formation of perchlorate.

Periodate

The periodates are in general significantly different from the perchlorates; on heating they are decomposed into iodates and oxygen. The periodates are produced by oxidation of iodates with chlorine or by anodic oxidation in either acidic or alkaline solution, but a low temperature and a low current density are desirable. All the periodates are slightly soluble in water: $CsIO_4$ is soluble to the extent of 2.15 g in 100 g of water at 15°C Cesium forms the only known salt of fluorinated periodic acid; no other fluorinated halogenates are known, nor are chlorinated iodates and bromates.

OXIDES

The following oxides of cesium are known: Cs_2O, Cs_2O_2, Cs_2O_3, and CsO_2 or Cs_2O_4.

Alkali metal oxides show an interesting gradation in stable types as the atomic weight increases. The ratio of oxygen to metal increases as the radius of metal increases; thus the stable oxide of cesium is the superoxide, CsO_2. It has the calcium carbide structure and should not be called tetraoxide.

The oxide, Cs_2O, vaporizes markedly at 250°C and tends to decompose into metal and the peroxide at high temperatures. Cesium upon burning in excess oxygen yields Cs_2O_4 which decomposes with difficulty upon heating to yield Cs_2O_3 and oxygen. Ammonia solutions of the metal are deep blue in color and when reacted with oxygen, a colorless or pale pink bulky precipitate settles out while the solution is decolorized. If the reaction is continued, the precipitate becomes a chocolate brown color and corresponds to the composition Cs_2O_3 at the maximum coloration. It is crystalline, melts upon heating and turns black; further oxidation yields yellow needles of Cs_2O_4. The peroxide is a strong oxidizing agent in the fused state and is decomposed by water with the formation of H_2O_2 and O_2.

HYDROXIDE

Cesium hydroxide, CsOH, can be easily prepared by metathesis of barium hydroxide and cesium sulfate; alternatively the cheaper slaked lime may be used,

$$Cs_2CO_3 + Ca(OH)_2 \rightleftarrows 2Cs(OH) + CaCO_3$$

Both of the above reactions are reversible, consequently, it is not possible to prepare the pure hydroxide in this manner. Electrolysis of cesium chloride is the principal method for preparation of pure hydroxide solution. The anode and cathode compartments are isolated from each other in various ways; the "diaphragm" method employs a porous cement or asbestos diaphragm, the "bell" method can be described as electrolysis in a "U" tube with 1 arm constituting the anode and the other the cathode so that no mixing occurs, and the "mercury" method consists essentially of plating cesium from brine into a mercury cathode on one side of a U-shaped apparatus and this then becomes an anode on the other side, from which cesium is stripped.

Cesium hydroxide is a highly deliquescent, crystalline solid (density = 4.018) readily soluble in H_2O with the liberation of much heat. The fused alkali attacks many metals due to the formation of small quantities of the free alkali oxide which combines with oxygen of the air to yield peroxide causing oxidation of the metal. Metals like platinum which have acidic oxides are particularly susceptible to attack.

When ozone is passed over solid CsOH, the white solid turns orange and fixes 2.2% of the oxygen. When the resulting compound is wetted, the fixed oxygen is given off as inactive oxygen not as ozone, and no H_2O_2 is given off upon solution. On standing, the orange color disappears and the yellow color of the peroxide remains. The aged substance yields H_2O_2 on treatment with H_2O indicating conversion to peroxide hydrates.

CESIUM PERMANGANATE

The permanganate salts of rubidium and cesium are prepared by adding the corresponding nitrates to a saturated solution of potassium permanganate at 60°C. On cooling, they crystallize out as the anhydrous salts. Cesium permanganate, $CsMnO_4$, is the least soluble of all the alkali permanganates, the solubility decreases with increasing atomic volume analogous to the behavior of the perchlorates. The properties of cesium permanganate are summarized in the Table III.

Table III

Density	3.55
Decomposition temperature	320°C
Solubility, g per 100 g	0.097 (1°C)
Saturated solution	0.23 (19°C)
	1.25 (60°C)

CHROMATE

Cesium chromate, Cs_2CrO_4, is the least soluble of the alkali metal chromates and resembles those of potassium and rubidium in being easily crystallized. The normal salts of these elements differ from that of sodium in that they dissolve more rapidly than the acid salts and yield the anhydrous salt.

PERMOLYBDATE

Cesium permolybdate, $Cs_2O \cdot 4MoO_4$, is distinguished by the fact that it is the richest in oxygen of all the salts formed with metal per-acids. It can be prepared by addition of H_2O_2 to a solution of the normal salt. All the alkali permolybdates are quite soluble but can be precipitated with alcohol.

SULFATES

Cesium sulfate, Cs_2SO_4, forms an anhydrous salt like those of NH_4^+, K^+, and Rb^+ and unlike those of Na^+ and Li^+. The solubilities (per 100 g H_2O) in this series increases with increasing atomic weight as follows:

Temperature	K_2SO_4	Rb_2SO_4	$(NH_4)_2SO_4$	Cs_2SO_4
0°	7.35 g	36.4	71.0	167
100°	24.1	81.8	97.5	220

Cesium Alums

Alums in general form a very characteristic group of double salts. The cesium alums have the formula, $Cs[M(SO_4)_2] \cdot 12H_2O$, where M may be many tervalent metals such as Al, Cr, Fe, Co, Rh, Ir, Mn, V, but not Bi, Tl, or rare earths. Also, sulfate in the alum may be replaced by selenate. All alums crystallize in the regular form, octahedra, which may grow to large size. Upon addition of various substances to the solution (urea, borax) the growth of the octahedral faces may be so repressed that cubical faces, or other faces of the regular system, may be formed. The solubility of the series of alkali alums decreases from sodium to cesium alum so that the latter has been used to isolate cesium from the mixtures of the alkali metals. Solubilities per 100 g of H_2O of some anhydrous alums are as follows:

Temperature	0°	30°	60°	Melting Point	
$KAl(SO_4)_2$	2.87 g	7.74	19.85	(92.5°)	54.45
$NH_4Al(SO_4)_2$	2.53	8.34	17.40	(95°)	52.20
$RbAl(SO_4)_2$	0.71	2.12	6.89	(109°)	58.5
$CsAl(SO_4)_2$	0.21	0.60	1.92	(122°)	62.0

The melting point is the transition point of the alum. It may be noted that this temperature increases in the direction K to Cs.

An increase in atomic volume of the anionic metal seems to favor the stability of the anionic complex. The tendency to lose water, and thus also the vapor pressure of the water of crystallization, rises with decreasing stability. The following table gives the temperature at which some cesium alums have a vapor pressure of 300 mm:

Anionic metal	Al	Ti	V	Cr	Fe
Atomic volume(x10^8 cm)	10.2	9.3	8.8	7.7	7.1
Dissoc. Temperature (°C) for 300 mm	96.52	92	85	84	76.5

Schonites

The cesium schonites correspond to the formula, $Cs_2M(SO_4)_2 \cdot 6\ H_2O$, in which the M may be any one of various bivalent elements such as Zn, Ni, Co, Fe, Cu, Mn, and V. They form isomorphous monoclinic crystals and are moderately soluble in water. A great variety of schonites can be prepared and they have, consequently, been studied in investigation of the effect of replacing atoms in a crystal lattice by other similar atoms. It was found that in formation of such analogous compounds from their elements, the percentage of contraction is always similar; but it is greater the more stable the compound. For cesium schonites the percentage contraction in the formation from the individual components is as follows:

Double sulfates of the type $Cs_2M(SO_4)_2 \cdot 6\ H_2O$

	Mg	Ni	Co	Fe	Cu	Mn	Zn	Cd
% Contraction	46.1	46.0	45.4	44.8	45.4	43.8	45.9	43.4

Persulfate

Cesium persulfate, $Cs_2S_2O_8$, is a sparingly soluble compound; the solubility of the persulfates diminishing in the series K-Rb-Cs-Tl. The compound, perdisulfuric acid, may be prepared by electrolysis of an acid ammonium sulfate solution; the reaction is as follows:

$$2HSO_4^- + \frac{1}{2}O_2 + H_2O \longrightarrow H_2S_2O_8 + 2OH^-.$$

In the presence of NH_4^+ a higher yield of the persulfate is obtained, and in the presence of Cs the cesium persulfate is precipitated.

Pyrosulfates

These compounds have the formula $M_2S_2O_7$ and may be regarded as a complex compound formed by elimination of one mole of water from two moles of sulfuric acid. The salts may be formed by heating the bisulfate, by heating the neutral sulfate with free SO_3 in a closed tube, or by recrystallizing the sulfate or bisulfate from warm concentrated sulfuric acid. The alkali pyrosulfates are best known; they dissolve easily, give up SO_3 on calcining, melt more easily than the sulfates (below red heat), and solidify in crystals from the melt. Cesium, potassium, and rubidium pyrosulfates are unlike those of sodium and the alkaline earths, in that they take up six more molecules of the acid oxide in liquid SO_3 and form crystalline compounds of the formula $M_2O \cdot 8SO_3$.

POLYSULFIDES

Sulfides of metals having large atomic volumes combine with more sulfur, giving polysulfides, which may be compared with the polyhalides. As in the polyhalides, the alkali metals, especially cesium, form the most stable compounds. Compounds of the alkali metals which range as high as M_2S_5 are known. The solid polysulfides are well crystallized substances, but all except Cs_2S_5 are very hygroscopic and are somewhat readily attacked by the oxygen of the air when moist. They are, of course, decomposed by water with the establishment of equilibria between sulfur and lower sulfides. The persulfides are decomposed by acids with the liberation of sulfur.

NITROGEN COMPOUNDS

Azides

The best method of preparing the salts of hydrazoic acid makes use of nitrous oxide as the source of the combined nitrogens $CsNH_2 + ON_2 \longrightarrow H_2O + CsN_3$. It is interesting to note, although it is not of practical importance, that alkali azides may be directly synthesized from the metal and nitrogen by reaction under the influence of the electric discharge. With K, Cs, and Rb, azides are formed accompanied by small quantities of nitrides as secondary products. The azide salts of the alkalis, alkaline earths, lead and the univalent heavy metals are all well known and resemble the halogen salts in many respects. The alkali azides do not explode even on percussion and may almost be melted without decomposition, as they explode only at high temperatures. The decomposition of alkali azides may be so arranged that it takes place gradually and gives a method for preparing pure nitrogen or pure metal. This is observed in the azide of cesium at about 350°C.

Nitrites

The property of nitrates of the alkalis of decomposing to nitrites is applied to their preparation: $2CsNO_3 \longrightarrow 2CsNO_2 + O_2$. The alkali nitrites are strong electrolytes, melt on heating to yellow liquids which decompose at higher temperatures, and hydrolyse to nitrous acid on boiling with water. The alkali nitrites form only very small crystals and are hygroscopic.

The stability of complex nitrites varies considerably. To the weak complexes belong the easily decomposed compounds: $Cs[Ag(NO_2)_2]$, $Cs_2[Ca(NO_2)_4]$, and $Cs_2Na[Bi(NO_2)_6]$ which serves for the quantitative determination of sodium or bismuth.

Nitrates

Nitrates are almost exclusively obtained by the action of the free acid on metals, oxides, or carbonates. All known nitrates dissolve easily in water. The solubility of ammonium and the alkali nitrates in decreasing order is $NH_4^+ — Na^+ — K^+ — Cs^+$. The alkali nitrates are anhydrous, melt and decompose on dry heating. The melting points of some nitrates, fusible without decomposition, are:

	NH_4NO_3	$LiNO_3$	$NaNO_3$	KNO_3	$CsNO_3$	$Ba(NO_3)_2$
Melting point	170°	264°	314°	339°	414°	592°

If several of these nitrates are mixed the melting point is depressed.

SALTS OF OXIDES OF PHOSPHOROUS

Hypophosphites ($H_2PO_2^-$)

All the salts of hypophosphorous acid are monobasic, easily soluble in water in contrast to the phosphates, and show reducing properties in solution. The alkali and alkaline earth salts are anhydrous or contain little water.

Phosphites ($PO_3^{=}$)

Phosphites of the alkalis are soluble in water, all others being very sparingly soluble; they are not amorphous like the phosphates, but crystalline like the hypophosphites, mostly with a definite water content.

Hypophosphates $(P_2O_6^{\overset{\equiv}{-}})$

The alkali salts are soluble in water; all other hypophosphates are difficultly soluble. The normal alkali salts are hydrolysed in water.

Phosphates $(PO_4^{\equiv})$

Only the phosphates of the alkalis and the primary salts of the alkaline earths are soluble in water. The solubility of the normal alkali phosphate increases with the atomic weight of the alkali, that of the phosphates of K^+, Rb^+, and Cs^+ being very considerable. On hydrolysis they are almost completely decomposed into the secondary phosphate and alkali hydroxide. The water of crystallization in the tertiary cesium phosphate is 5 moles; in the secondary salt it is 1 mole.

Pyrophosphates $(P_2O_7^{\overset{=}{=}})$

The pyrophosphates are obtained only in two stages of neutralization - as quaternary and secondary salts $M_4P_2O_7$ and $M_2H_2P_2O_7$. The alkali salts are soluble in water; the quaternary alkali salts are slightly hydrolysed.

CARBONATE

Carbonates may be regarded as complex anionic compounds of the metallic oxide and carbon dioxide of the type $M[O(CO_2)]$, and the carbonates of comparable metals are more stable the greater the volume of the cation. In the series of alkali carbonates there is an exception to the above stability, for the dissociation of potassium carbonate is least, and it then increases to cesium carbonate. At 1200°C the alkali carbonates show the following dissociation pressures:

	Li_2CO_3	Na_2CO_3	K_2CO_3	Rb_2CO_3	Cs_2CO_3	
ca	300	41	27	60	95	mm Hg

Carbonates are strongly hydrolyzed in solution, and even those of the alkali carbonates are largely decomposed with formation of the alkali hydroxides. The normal alkali carbonates and that of thallium are somewhat soluble; the acid carbonates are less soluble and are therefore precipitated from saturated solutions of the normal salts by passing in carbon dioxide. The normal carbonates of potassium, rubidium, and cesium are deliquescent in air, while the acid salts are unchanged.

ANALYTICAL METHODS

The analytical methods utilized to separate and/or determine cesium isotopes are listed in Tables IV, V, VI and VII.

Table IV - Precipitation Methods

Precipitant	Sample	Technique	Comments	References
Alum	Water, prepared organic samples	Radiochemical	Separates Cs from bulk alkali elements and mixed F.P.	32,97
Bismuth iodide	Fission product, alkali solutions	Radiochemical, gravimetric	99% Recovery $Cs_3Bi_2I_9$	58,60
Chloroplatinate	Fission product, alkali solutions	Radiochemical, gravimetric	Precipitates K, Rb, Cs NH_4	32,79,88 91,92,97 100
Cobaltinitrite	Low conc. F.P. in H_2O or aqueous solutions containing alkali	Radiochemical, gravimetric, carrier-free	Cs:K:Na:Co ratio in ppt 0.1:2.0:0.9:1.0	42,64,77
Silver bismuth nitrite	Alkali solutions	Gravimetric	Specific for Ru and Cs	36,37
Sodium-lanthanum nitrite	Alkali solutions	Gravimetric down to 3 mg Cs	Accuracy ±0.2%, Rb and K do not precipitate	21
Dipicrylamine	Fission product, aqueous solution	Radiochemical, gravimetric (5-200 mg conc. range)	Radioactive Cs carries on both Cs and K dipicrylamine ppt.	30,50,80
Thallium (I) Dipicrylaminate	Fission products	Carrier-free	Carrier-free Cs can be extracted from precipitate. 90% recovery of active Cs.	101

Perchlorate	Fission products	Radiochemical	Large amounts K,NH_4 Na, and Rb interfere.	42,62,92
Permanganate	Aqueous solutions	Gravimetric	Solubility product at 1°C is $1.5x10^{-5}$. Rb coprecipitates.	11
Phosphomolybdate	Low conc.F.P. in H_2O	Radiochemical	Cs:NH_4:P:Mo ratio in ppt 1.8:1.2:1.0:12.0 93% recovery.	42
Silicotungstate	Fission products	Radiochemical	Separates Cs from alkali metals.	42,62,91
Stannic bromide	Alkali solutions	Gravimetric	Cs_2SnBr_6 precipitate.	22
Tetraphenylboron	Fission products	Radiochemical	Macro amounts of Rb and K interfere.	28,31

Table V - Carrier-Free Methods

Concentration	Sample	Technique	Comments	References
Tracer Cs isotopes	Fission products	Coprecipitate with thallium (I) dipicrylaminate	Active Cs extracted into 2 N HCl.	101
Tracer Cs isotopes	Fission products	Coprecipitate with NH_4ClO_4	High purity Cs tracer obtained.	63
Tracer Cs isotopes	Fission products	Coprecipitate with ammonium cobaltinitrite	<0.5% radioactive contamination of tracer Cs isotopes.	64
Tracer Cs^{131}	Irradiated Ba	$BaCl_2$ precipitation.	Radiochemically pure Cs^{131} obtained.	48,61
$\sim 10^{-7}$ to 10^{-3} M Cs	Purex type and TBP-25 type wastes	Solvent extraction using 0.2 M I_2 in nitrobenzene	Extraction coefficients 10-20 at 25°C.	53
Tracer to 10 mg Cs	Fission products	Tetraphenylboron extraction	See procedure 8.	23

Table VI - Ion Exchange and Chromatographic Methods

Resin	Sample	Eluant for Cs	Comments	Reference
Amberlite IRA-400(OH)	F.P. in acid	H_2O	Sr,Cs eluted. F.P. held.	18
Deacidite FF	F.P. in acid -pH 1	None	Cs isotopes pass thru.	95
Dowex-1	F.P. in acid	None	Alkali metals pass thru.	5,57
Dowex-1	F.P. in 0.5% NH_4Cl	None	Cs + Sr^{90} pass thru.	99
Dowex-1	Alkali metals in EDTA	None	Effluent order Cs-Na-Li.	65
Dowex-2	Mixed F.P. in H_3PO_4	None	Cs, Te(IV) isotopes pass thru.	24
Dowex-50	F.P. in HCl and HNO_3	0.50 N NH_4Cl	Cs isotopes eluted.	94
Dowex-50	Alkali chlorides in H_2O	0.3 N HCl	Cs + few % Rb eluted.	13
Dowex-50	Low conc. F.P. in H_2O	6 N HCl	99.7% Cs recovery.	42
Duolite C-3	High conc. alkali salt solution, Cs + 10^4 Na + 5Rb	6 N HCl	Cs + trace K + trace Na+ <2 ppm Rb eluted.	76
Duolite C-3	Cs fraction separated from F.P.	3 N HCl	Separates Cs isotopes from K and Rb	85
IR-1	Activated alkali metals	0.1 N HCl	Effluent order Na-K-Rb-Cs	8
Paper chromatography	Separated K-Rb-Cs fraction		Estimates 5 to 1000 μg of each cation. No interference from 1 mg Na,Li,Ba, Cs,Sr,Mg.	54
Paper chromatography	Fission products		See Radiochemical Method 10	15,16

Table VII - Spectrochemical Methods

Method	Sample	Spectral Lines Å	Determination Limit	Accuracy	Comments	Ref's
Arc excitation	Uranium base materials	8521	8 ppm		Carrier-distillation method. Ga_2O_3 carrier.	78
Arc excitation	Silicates	8521	~2 ppm	~5%	Methods for Na and K internal standards and for no internal standard are discussed.	2
Hydrogen-Oxygen Flame	Aqueous	8521	~1 ppm	~1%	Spectrophotometer designed for radioactive samples.	44
Hydrogen-Oxygen Flame	Glass, Ores	8521	~1 μg		Samples decomposed and dissolved in~0.02 N HCl.	93
Image-Converter Flame	Bi-U Alloys	4555,8521	0.2-5%	5-10%	Better precision with 8521 A line.	90
Mass Spectrometry	Cs Isotopes	Isotopic Analysis			Cs isotopes obtained from fission product samples.	57

IV. Dissolution of Samples Containing Compounds of Cesium

A prime requisite when dissolving radioactive samples for subsequent determination with carrier is complete exchange between the radioactive isotope and the carrier. Since cesium exists in only one oxidation state, there is complete, rapid exchange. Another requisite is that the isotope remain in homogeneous solution until analyzed. Cesium, when present in solution in extremely low concentrations, adsorbs on the walls of glass and plastic containers. Crouthamel, et al.(16) have reported that over 50% of carrier-free cesium-137 in 2 M HCl or 2 M HNO_3 has been lost from solution after one month, and that the addition of approximately 1 μg cesium carrier per ml has stabilized these solutions for a period of six months. Radiochemists generally analyze for cesium isotopes in the following types of samples: irradiated nuclear fuel, activated cesium salts, natural water sources, organic materials, and agricultural materials.

The dissolution of irradiated nuclear fuel elements presents many problems when using cesium-137 as a burn-up monitor. It is very important that the section dissolved is representative of the entire fuel element sample. In cases where the neutron flux varies for different parts of the sample, the entire sample should be dissolved or sufficient samples run to determine a burn-up map. Precautions must also be taken to prevent loss of cesium and its volatile parent xenon. The degree of burn-up, temperature, porosity of the fuel, and permeability of container are important factors in this containment problem. Rider(75) reported two experiments which indicate the necessity for dissolving the container in addition to the sample. When a small UO_2 piece was irradiated under NaK, 75% of the cesium-137 leached out of UO_2 relative to gross gamma measurements. Second, when U_3O_8 was irradiated in platinum capsules, cesium-137 and other fission products were driven into the platinum to sufficient depth that only complete dissolution in aqua regia effected complete recovery.

Fuel element samples are generally dissolved in volatile acids such as HCl, HNO_3, HF, or combinations of these acids, containing a small amount of inactive cesium. Uranium metal, UO_2, and U-Mo alloys have been dissolved in concentrated or 8 N HNO_3, gradually heated in glass beakers.(46,75) U-Th alloys have been dissolved in concentrated HNO_3 containing a few crystals of ammonium bifluoride.(46) Other U alloys (Al, Zr, Mo, etc.) have been dissolved in aqua regia containing 2% fluoboric acid while heating gradually.(75) Zircalloy, stainless steel, and other metallic clad fuel elements have been dissolved in acids in a similar manner.

Since all cesium salts dissolve in water and dilute acids, their solution is simple. Natural water sources generally contain very small amounts of cesium isotopes requiring concentration of the sample by either of the following methods. The preferred method is to pass the sample through a cation-exchange resin column and then to elute the cesium with 6 M HCl.(41,42,98) If large concentrations of other ions interfere with the ion-exchange method, then precipitation methods can be used. Cesium can be precipitated as cesium ammonium phosphomolybdate(42) or coprecipitated with sodium potassium cobaltinitrite.(42,85,98)

Organic materials, such as tissue, human urine, and blood, can be decomposed with HNO_3 in the presence of carrier and, following destruction of the organic matter, the cesium can be extracted with water or acid (see procedure 7).(97,102,103) Cereals, dried vegetables, and dry milk can be dry ashed at 400-450°C, and the cesium extracted with hot HCl (see procedure 7),(102,103) or hot HNO_3.(97) Soils are generally treated with M ammonium acetate, the extract evaporated, the organic matter decomposed with HCl or aqua regia, and the cesium extracted.(102,103) Cesium has also been leached from soil samples with IN HNO_3,(29) 3 N HCl-0.1 N HF, (27) or 9 M H_2SO_4.(40) The naturally occurring cesium in soils must be accounted for when determining recovery values.

V. Counting Techniques for Use with Isotopes of Cesium

The methods of measurement of the radioactivity of nuclides vary with the properties of the radiations emitted by the nuclides. Such factors as half-life, type of radiation, and energy of radiation must be considered. The nuclear characteristics of the isotopes of cesium can be found in the literature(68,84) and are summarized in Section II.

References for counting techniques should be consulted for details of the methods. Surveys of general methods for the measurement of radioactive sources are given by Mann and Seliger(52) and by Steinberg.(83) The technique of gamma-ray scintillation spectrometry has been described by Heath(33) and Olson.(69) Absolute calibration of scintillation crystals has been discussed by Bell.(81) Pate and Yaffe(70,71) have described the $4\pi\beta^-$ counting technique for determining absolute disintegration rates.

The isotopes of cesium from cesium-123 through cesium-132 have relatively short half-lives and are not generally encountered. Stable cesium-133 (σ 0.016 + 31 barns) can be activated by thermal neutrons to produce cesium-134 m and cesium-134. The preferred methods for the routine assay of cesium-134 are $2\pi\beta^-$ windowless counter and well-type scintillation counter.(51) Pure cesium-134 has been standardized by gamma-ray spectrometry using 800-kev gamma photo-peak.(45)

Fission product yields of cesium isotopes with half-lives longer than one hour are listed in Table VIII:(43)

Table VIII

	%Yield-Thermal-Neutron Fission			%Yield-Fast-Neutron-Fission			
Isotope	U^{233}	U^{235}	Pu^{239}	U^{235}	U^{238}	Pu^{239}	Th^{232}
stable Cs^{133}	5.78	6.59	6.91		5.5		
2.6×10^{6} y Cs^{135}	6.03	6.41	7.17		6.0		
13 d Cs^{136}	0.12	0.0065	0.11				
30 y Cs^{137}	6.58	6.15	6.63	6.3	6.2	6.8	6.3

Cesium-135 is a single β^- emitter and has a long half-life and high fission yield. Its large thermal cross-section ($\sigma \sim 15$ barns) and that of its parent Xe^{135} (σ 3.2×10^{6} barns) reduces the cesium-135 concentration in case of irradiations for long periods of time.

The cesium fraction from young mixed fission products has been analyzed for cesium-136 and cesium-137 with a multichannel gamma-ray spectrometer.(31) This technique is described more fully in Procedure 4. A mixture of cesium-134 and cesium-137 can generally be found in the separated cesium fraction from a long irradiated fuel element, cooled sufficiently so that cesium-136 is absent. The cesium-134 is produced by neutron capture by cesium-133 formed by fission or present as contamination. Cesium-134 in such mixtures has been determined by gamma-ray spectrometry.(45) Cesium-137 has been determined by means of the conversion x-ray spectra(45) and by gamma-ray scintillation spectrometry.(4,16)

Cesium-137 (barium-137m) has a long half-life, low neutron capture cross-section ($\sigma < 2$ barns), high fission yield, and simple decay scheme (Fig. I). The preferred methods for the routine assay of pure cesium-137 are $2\pi\beta^-$ windowless counter and well-type scintillation counter.(51) Several methods for determining

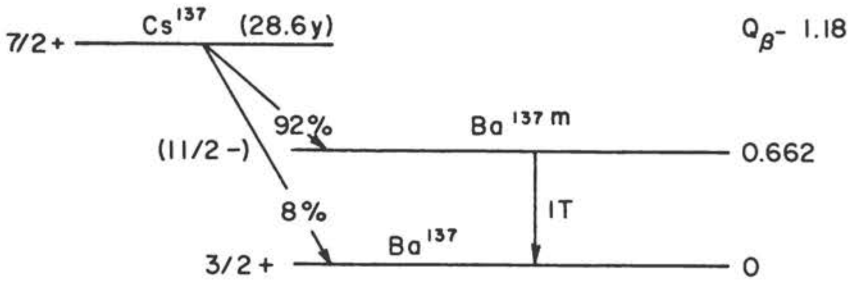

Figure 1 - Decay Scheme of Cesium-137

cesium-137 by gamma-ray scintillation spectrometry have been reported.(5,49,96) The disintegration rate of pure cesium-137 samples can be obtained by evaporating aliquots, free of solids, on gold-coated Vyns films and $4\pi\beta^-$ counting. The counts must be corrected for the 10.5% conversion of the 662 kev gamma ray of barium-137 m to determine the absolute disintegration rate.

Cesium-137 (barium-137m) liquid standards are available from Nuclear-Chicago Corporation. They are prepared in a manner which duplicates the methods previously used by the National Bureau of Standards.

Cesium-137 has been used as a fission monitor.(16,17) Physical constants are of primary concern when using an isotope as a fission monitor. The Fuel Burnup Group, Dosimetry Task Force, A.S.T.M., has therefore suggested the following constants for cesium-137: 6.15% yield of cesium-137 from thermal-neutron fission of U^{235}, 28.6 year half life, 10.5% internal conversion of the 662 kev gamma ray, and 92% branching ratio for beta decay.(6)

The gamma radiation emitted by all human beings indicates the presence of cesium-137. Miller(55) describes equipment and techniques developed to study the metabolism of gamma ray emitting elements in the intact, healthy, human body.

VI. Applications of Radioisotopes of Cesium

Radioisotopes exhibiting radiation characteristics suitable for nuclear gages and other types of nondestructive testing equipment are limited in number, the principal ones being strontium-90, thallium-204, krypton-85, cobalt-60, cesium-137, and iridium-192. The cesium-137 isotope, with its 510 kev beta in equilibrium with the 662 kev gamma of barium-137m is used for beta gaging of light materials, reflection and density gages, and radiography.

There are several papers on the development of thickness gages which measure either the absorption or scattering of betas and gammas of cesium isotopes.(14,39,73,87) A precision density gage for use under field conditions is described in the literature.(1) A combination of a cesium-137 density gage and a mass-flow meter is utilized in a system for obtaining true mass flow.(1) A method to control large differences in height levels utilizes the backscattering of the gamma rays of cesium-137.(87) A gage, incorporating a cesium-137 gamma-ray source, can measure soil densities with an accuracy of about 1% and can be used at depths down to 1000 feet.(12) Other applications of thickness gages include studies of thickness or density preparatory to construction of highways and buildings, inventory of large stockpiles of materials, continuous measurement of the weight of products, and other process and quality control uses.

A gamma milker using ion exchange separation has been developed to separate the short-lived barium-137 m from its long-lived parent cesium-137.(66) The daughter product has many industrial applications measuring leakage in heat exchangers, flow characteristics of large pipes or streams, and flow velocities of liquids.

A technique to measure flow rates of condenser water, petroleum stocks circulating in and between units in a refining plant, waste refinery water in open ditches, natural creeks and rivers utilizes the total-count method of the cesium-134 isotope.(35)

Isotopes, in order to be useful in industrial radiography, must have suitable radiation spectra, reasonably long half-life, and be economically produced at high specific activities. Cesium-134 has been evaluated for use as a gamma ray source for industrial radiography.(19) It is suitable on the basis of gamma radiation energy, satisfactory half-life, and specific activity, but its cost per curie makes it economically unacceptable.

Cesium-137 is a very suitable gamma radiographic source. Dutli and Taylor(20) compare its radiographic characteristics with those of cobalt-60 and 1000 pkv x-rays. Data on the exposures required in the radiography of steel, iron, and aluminum using cesium-137 and other sources have been reported.(3) Cesium-137 gives a 2% sensitivity when radiographing steel in the thickness range of 3/4 to 3 1/2 inches.(74) Various techniques have been explored and sensitivity curves are reported for the inspection of welds in ship structures using isotopes of thulium-170, iridium-192, cesium-137, and cobalt-60.(72)

A major medical application of radioactivity is in teletherapy devices. Cesium-137 is considered a good teletherapy source because its long half-life makes repeated calibration of equipment unnecessary, and it has more favorable radiation protection requirements than the more commonly used cobalt-60 sources. Brucer(9) evaluates cesium-137 as such a source. The design and utilization of teletherapy apparatus and the medical uses of cesium-137 sources are dealt with in a National Bureau of Standards Handbook.(59) Recent advances in teletherapy are reported by Brucer and Simon.(10)

Baarli(7) has reported on a plesiotherapy unit (short source-skin-distance, SSD, as compared to long SSD in teletherapy) using a 50-curie cesium-137 source. It is useful for treatment of some cancers. Gauwerky(26) describes the preparation and use of cesium-137 applicators for the treatment of cancer by local application.

VII. Collection of Detailed Radiochemical Procedures for Cesium

Procedure 1: Perchlorate Method. Paper 283 by L. E. Glendenin and C. M. Nelson, Nat. Nuclear Energy Ser., Div. IV, 9, Book 3, 1642-5 (1951).

Procedure

Step 1. Add 2 ml of Cs carrier (ca. 25 mg CsCl) and 5 ml of 70% $HClO_4$ to the fission product solution in a 50 ml centrifuge tube (note 1). Evaporate solution until dense white $HClO_4$ fumes evolve. Cool the solution under tap water, add 15 ml absolute ethanol, and cool the solution for 2 minutes with stirring. Centrifuge and wash 2 times with 10 ml absolute ethanol.

Step 2. Dissolve precipitate in 10 ml H_2O, heat solution to incipient boiling and add 5 mg Fe^{+3} carrier. Precipitate $Fe(OH)_3$ by dropwise addition of 6 N NH_4OH with stirring (note 2). Centrifuge and discard precipitate. Repeat precipitation by addition of 5 mg Fe^{3+} carrier. Centrifuge and discard precipitate.

Step 3. Add 5 drops of 6 M NaOH and evaporate solution to 5 ml (note 3). Add 4 ml of 70% $HClO_4$ and evaporate solution by swirling over a burner until appearance of $HClO_4$ fumes. Cool solution under tap water, add 15 ml absolute ethanol with stirring, and cool for 1-2 minutes.

Step 4. Filter precipitate onto a weighed filter paper (note 4) in a small Hirsch funnel and wash 3 times with 5 ml absolute ethanol. Dry for 10 minutes at 110°C, weigh precipitate as $CsClO_4$, and mount on a card, cover, and count with an end-window beta counter.

Notes

1. In the presence of K^+, NH_4^+, large amounts of Na^+ (>0.5 g) or Rb^+ activities, cesium can be first separated by precipitation as cesium silicowolframate, $Cs_8SiW_{12}O_{42}$. Add 2 ml Cs carrier and 20 ml 6 M HCl to the sample in a 50 ml centrifuge tube. Add 1 ml 0.13 M silicowolframic acid, $H_8SiW_{12}O_{42}$, and allow solution to stand with occasional stirring for 5 minutes. Centrifuge solution and wash precipitate twice with 10 ml 6 M HCl. Dissolve precipitate in 1 ml 6 M NaOH and add 5 ml 70% $HClO_4$. Evaporate solution by swirling over a burner to fumes of $HClO_4$ and then boil gently for about 2 min. Cool solution, dilute to 10 ml, and centrifuge. Discard the precipitate of Si and wolframic acid. Treat supernate by the regular procedure starting with the evaporation in Step 1.

2. No more than 5 drops 6 M NH_4OH are usually required.

3. Remove traces of NH_4^+ by boiling with NaOH. Test for complete removal by adding another 1 or 2 drops 6 M NaOH, boil, and test the vapor with litmus paper. Store 6 M NaOH in waxed glass or hard rubber bottle to keep it free of silica.

4. Wash filter-paper disk with ethanol and dry under the conditions of the procedure before weighing.

Procedure 2: Chloroplatinate Method. Report by B. F. Rider,
Vallicitos Atomic Laboratory, Pleasantville, Calif.

Procedure

Step 1. Add 1 ml standardized Cs carrier (20 mg/ml), 10 ml H_2O, 5 drops Fe carrier (10 mg/ml), and one drop each of Ru, Zr, and Ce carriers (10 mg/ml each) to an aliquot (usually 100 λ) of the fission product solution in a 50 ml centrifuge tube.

Step 2. Add 3 drops thymolphthalein indicator (0.1% in ethanol) and add 1 N NaOH while swirling until the blue end point is reached.

Step 3. Centrifuge the solution and decant the supernatant through an 11 cm Whatman #40 paper into a clean centrifuge tube.

Step 4. Add 2 ml 5% chloroplatinic acid, $H_2PtCl_6 \cdot 6\ H_2O$, and swirl and heat the solution in a beaker of boiling water to coagulate the precipitate.

Step 5. Centrifuge solution and discard supernatant.

Step 6. Slurry precipitate with H_2O onto weighed, dried 2.4 cm filter paper and wash with water.

Step 7. Dry precipitate at 135°C for 15 min., cool in a dessicator, weigh as Cs_2PtCl_6 and count on a gamma spectrometer.

Counting Method

1. Scan each plate on a 256 channel analyzer. Compare the 660 kev peak height of the sample with that of a Cs^{137} standard precipitated as Cs_2PtCl_6 and mounted in the same manner. Small

traces of Ru^{106} or Zr^{95} that are occasionally found are eliminated in this manner (note 1).

2. When Cs^{134} is present, it is subtracted out by complementing the spectrum on the 256 channel analyzer and inserting a pure cyclotron-produced Cs^{134} spectrum in the subtracting direction until the 0.8 Mev peak just disappears. Correction can be made to a few per cent.

3. Cs^{136} correction is not usually applied since samples have usually been cooled 60 or more days. The Cs^{136} decays to about 1/32 in 65 days. The spectrum of a Cs sample taken soon after irradiation is complicated, and gamma ray spectrum analysis is only partially successful. Cs^{136} yield is a thousand fold less than Cs^{137}, so both are of comparable decay rates at first.

Notes

1. Lacking an analyzer an additional preliminary step is included in the procedure, probably a preliminary $CsClO_4$ precipitation. Final counting is for gross gamma.

Procedure 3: Chlorostannate Method. Report by W. S. Lyon, Oak Ridge National Laboratory, Oak Ridge, Tennessee.

Procedure

Step 1. Add 2 ml standardized Cs carrier (10 mg CsCl/ml), 1 ml Fe holdback, 2 ml concentrated HCl, and an aliquot of the sample to a 50 ml centrifuge tube and evaporate nearly to dryness.

Step 2. Dissolve the residue in 1 ml H_2O. Add 10 ml 1:2 HCl-C_2H_5OH and heat the solution to boiling.

Step 3. Add 5 ml boiling $SnCl_4$ (1:2 HCl-C_2H_5OH saturated with $SnCl_4$) reagent and allow the tube to cool.

Step 4. Centrifuge solution and discard the supernatant. Wash the precipitate with 10 ml 1:2 HCl-C_2H_5OH.

Step 5. Dissolve precipitate by heating in 3 ml H_2O. Add 1 ml Fe holdback and 5 ml 1:2 HCl-C_2H_5OH. Repeat Step 4.

Step 6. Slurry the precipitate in a few ml 4% HCl-C_2H_5OH, filter on a tared paper, and wash with HCl-C_2H_5OH and ether.

Step 7. Dry the sample, weigh as Cs_2SnCl_4, transfer to a 10 x 75 mm glass culture tube and count on a "cheater" scintillation counter (note 1).

Counting Method

1. Count the sample on a single channel analyzer set on the 660 kev peak to minimize contributions from Cs^{134} and Cs^{136} which are usually very low.
2. Compare the sample with two Cs^{137} standards.

Notes

1. Rb^+ or large amounts of K^+ or NH_4^+ in the original solution interfere with the analysis.
2. The over-all accuracy of the method is believed to be 10% or better.

Procedure 4: Tetraphenylboron Precipitation Method. Paper on Determination of Radioactive Cesium by T.H. Handley and C.L. Burros. Oak Ridge National Laboratory, Oak Ridge, Tennessee. (Anal. Chem. 31, 332-4, (1959))

Procedure

Step 1. Add 1 ml Cs carrier (ca. 6.5 mg CsCl/ml) and about 5 mg of Fe, Ba, La, and Zr carriers to an aliquot of the sample containing Cs (note 1). Dilute the solution to 15 ml and add 1 M NaOH until just basic to phenolphthalein. Add 1 ml 3 M Na_2CO_3 and warm the solution to coagulate the precipitate. Centrifuge and discard precipitate.

Step 2. Make supernate just acid with 6 M HCl and add 5 mg each of Fe, Ba, La, and Zr carriers. Repeat hydroxide and carbonate precipitation.

Step 3. Make supernate just acid with 1 M HCl and cool in an ice bath. Add dropwise while stirring 1 ml of $NaØ_4B$ solution (note 2) and allow solution to stand for 10 minutes. Centrifuge solution and discard supernate. Wash precipitate with 5 ml H_2O, centrifuge and discard wash solution.

Step 4. Dissolve precipitate in a minimum of acetone and add 1 ml 1 N HCl. Dilute solution to 10 ml with water and cool. Add dropwise 4 ml $NaØ_4B$ solution and allow solution to stand for 10 minutes. Centrifuge solution and discard supernatant. Wash precipitate with water and discard supernatant.

Step 5. Dissolve precipitate in a minimum of acetone, usually 1 ml; add 10 ml of absolute alcohol containing 0.5% by weight of $NaØ_4B$ and cool the solution in an ice bath for 10 minutes with occasional stirring. Filter precipitate onto a tared No. 42 Whatman or a Munktell No. 00 filter disk and wash with several small portions of alcohol. Dry precipitate at 110°C for 15 minutes and weigh as a $Cs\phi_4B$ (note 3). Mount precipitate for beta counting or place in a suitable tube for gamma counting.

Counting Method

1. In old mixed fission products Cs^{137} is the only cesium radionuclide present. Count cesium in a well type scintillation counter previously calibrated with a Cs^{137} standard.

2. Count samples from young mixed fission products that contain Cs^{136} and Cs^{137} on a multichannel gamma-ray spectrometer. Determine Cs^{136} by integration of the 1.04 Mev photopeak following subtraction of Compton distribution from the 1.25 Mev photopeak. For calculation assume that Cs^{136} decays 100% through the 1.04 Mev gamma. Determine Cs^{137} by integration of the 0.662 Mev photopeak following subtraction of the Compton distribution from the 1.25, 1.04, and 0.82 Mev gammas. Count radionuclides of nearly the same energy under identical conditions to establish the correct Compton distribution for subtraction from the spectrum of the unknown. For the 0.82 Mev peak use a standard of Mn^{54}. For the 1.04 Mev peak use Zn^{65} and for the 1.25 Mev peak use Na^{22}. A factor of 0.82 was used for calculating the disintegration rate of Cs^{137}. This factor includes correction for branching and internal conversion of the 0.662 Mev gamma of Cs^{137}. To obtain the disintegration rate use is made of photopeak-to-total-ratio as a function

of gamma-ray energy and source distance.(1,2) The disintegration rate of a specific radionuclide is given by the following relationship:

$$\text{Disintegration Rate} = \frac{N_p D}{E_t\ P\ A\ B\ Y}$$

N_p - integrated area under photopeak

D - dilution factor

E_t - total absolute detection efficiency for source detector geometry used

P - appropriate value for peak-to-total ratio

A - correction factor for absorption in source and any beta absorber used in measurement

B - correction for branching ratio and internal conversion of the gamma measured

Y - chemical yield.

Notes

1. In the presence of macro amounts of Rb and K, add 1 ml standardized Cs carrier, 15 ml 6 M HCl, and 2 ml silicotungstic acid, $H_8SiW_{12}O_{42}$, (1 g/ml) to an aliquot in a 50 ml centrifuge tube. Digest the sample for 10 minutes, centrifuge, and discard supernatant. Wash precipitate with 5 ml 6 M HCl. Dissolve $Cs_8SiW_{12}O_{42}$ precipitate in 1/2 ml 6 M NaOH (warm, if necessary); add 20 ml 6 M HCl and discard yellow precipitate. Add 2 ml $H_8SiW_{12}O_{42}$. Digest sample for 10 minutes, centrifuge, and discard supernatant. Wash precipitate with 5 ml 6 M HCl. Dissolve precipitate in 1/2

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1) Heath, R.L., IDO 16408, (July 1957)

2) Bell, P.R., Davis, R.C., Lazar, N.H., ORNL Rept. 72 (1957)

ml 6 M NaOH. Begin Step 1 of regular procedure, omitting the addition of Cs carrier.

2. Prepare $Na\phi_4B$ solution by dissolving 4 g $Na\phi_4B$ and 1 g $AlCl_3 \cdot 6\ H_2O$ in 100 ml H_2O. Add a few drops phenolphthalein indicator solution. Add 6 M NaOH dropwise until the solution is just alkaline. Allow solution to stand several hours, filter, and dilute to 200 ml. Store solution in a refrigerator where it will keep for several months.

3. The chemical yield is usually 75% or better. A decontamination factor $\geq 10^6$ was obtained for each radionuclide tested and for mixed fission product solutions.

Procedure 5: Bismuth Iodide Method for the Determination of Cesium Activity in Fission. Paper 284 by H.B. Evans, Nat. Nuclear Energy Ser., Div. IV, 9, Book 3, 1646-8 (1951).

Procedure

Step 1. Add 20 mg standardized Cs carrier (1.263 g CsCl/100 ml in H_2O standardized by chloroplatinate method[1]), 20 mg Rb carrier (1.414 g RbCl/100 ml in H_2O), 5 mg each of Ce, Y, La, Zr, Ba, and Sr carriers (note 1) to the sample of fission material (note 2). Add 12 N NaOH until the solution is basic to phenolphthalein and then 1 ml 1 M Na_2CO_3. Centrifuge and discard precipitate.

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[1] Scott, W.W., Standard Methods of Chemical Analysis, 5th Ed., Vol. I, p. 869, D. Van Nostrand Co., Inc.

Step 2. Acidify supernatant solution with concentrated HCl, add about 10 mg La carrier, and then add 12 N NaOH to make solution basic to phenolphthalein. Centrifuge and discard precipitate.

Step 3. Make supernatant solution acid with glacial $HC_2H_3O_2$ (note 3) and then add 1 ml HI-BiI_3 reagent (note 4). Cool for several minutes (note 5) and centrifuge. Supernatant solution can be used for Rb analysis.

Step 4. Wash precipitate with 7 ml H_2O and 1 ml 2 M HCl, keeping solution cool. Centrifuge and dissolve precipitate in 6 drops conc. HCl by heating to boiling. Add 10 mg Rb carrier and 1 ml H_2O. Cool and add 1 ml HI-BiI_3 mixture. Allow to stand several minutes and centrifuge.

Step 5. Wash precipitate with cold 2 M HCl, filter onto weighed filter-paper disk, and wash successively with 5 ml portions of absolute ethanol and ether. Dry at 110°C. for 10 minutes and weigh as $Cs_3Bi_2I_9$ (note 6).

Notes

1. Sample may contain either U or Pu as either nitrate or chloride (sulfate solutions have not been tested). First precipitation removes bulk of the U or Pu.
2. Addition of these carriers aids in removal of fission-product cations.
3. If the volume exceeds 15 ml, it is best to evaporate the solution to this volume.

4. The HI-BiI_3 is prepared by dissolving 10 g BiI_3 in 50 ml 55% HI. Presence of some free iodine does not interfere with the precipitation.

5. Precipitate of $Cs_3Bi_2I_9$ forms quite rapidly and is very insoluble in cold dilute HCl or $HC_2H_3O_2$.

6. If greater decontamination from other fission elements is desired, the $Cs_3Bi_2I_9$ is dissolved and the Cs is reprecipitated as Cs_2PtCl_6 according to the following scheme: Dissolve $Cs_3Bi_2I_9$ precipitate from Step 5 of above procedure in about 2 ml 6 M HNO_3. Boil to remove I_2, add 1 ml conc. HNO_3 and 3 ml H_2O, and cool the solution. To the cool solution add 10 ml ethanol (solution should remain cool), 0.5 ml 0.5 M H_2PtCl_6, and 7 ml more alcohol. Wash Cs_2PtCl_6 with alcohol, filter onto filter-paper disk of Whatman No. 50 paper, wash with ether, dry at 110°C. and weigh as Cs_2PtCl_6.

7. Method provides a decontamination factor $>10^4$ from other fission activities if Cs is reprecipitated as $Cs_3Bi_2I_9$; a decontamination factor $>10^5$ if Cs is reprecipitated as Cs_2PtCl_6.

Procedure 6: Phosphotungstate Precipitation Method of Analysis of Radioactive Cesium in Solutions of Long-Lived Fission Product Activities by E. Mizzan, Chalk River Atomic Energy of Canada Limited (PDB-128)(1954).

Procedure

Step 1. Pipette aliquot of aqueous solution of the long-lived fission product activities into a 12 ml centrifuge tube containing

6 drops Cs carrier (12.7 g CsCl in 1 liter H_2O), 1 drop Ru carrier (20.5 g $RuCl_3$ in 1 liter H_2O), and 0.5 ml Zr carrier (29.4 g $ZrO(NO_3)_2 \cdot 2H_2O$ in 1 liter H_2O).

Step 2. Dilute to 8-10 ml with 5 N HNO_3 and add with stirring 1 ml 0.05 M phosphotungstate acid (66.2 g $P_2O_5 \cdot 24\ WO_3 \cdot 25H_2O$ in 400 ml H_2O) (note 1).

Step 3. Let stand 5-10 minutes, centrifuge, and discard supernatant.

Step 4. Wash precipitate thoroughly with 8-10 ml 5 N HNO_3, centrifuge, and discard supernatant.

Step 5. Repeat Step 4.

Step 6. Slurry precipitate with 3-4 drops H_2O and transfer completely by means of a spitzer onto an aluminum disc. Rinse centrifuge tube and spitzer with small portions of H_2O and place on the disc.

Step 7. Dry precipitate under an infra-red lamp.

Step 8. Dry precipitate further on Ful-Control heater for about 30 seconds (note 2).

Step 9. Count with a G.M. end-window counter (note 3).

Notes

1. Wash stirring rod free of any precipitate by fine stream of water before removing from centrifuge tube.

2. Heat precipitate at full heat until orange-yellow coloration appears - about 30 seconds.

3. No radiochemical yield, self-absorption and self-scattering are required. The Cs recovery is complete and the amount of inactive Cs carrier is so chosen that the self-scattering and self-absorption effects cancel each other.

4. Decontamination from other long-lived fission product activities is satisfactory.

Procedure 7: Separation of Radioactive Cesium in Biological Materials. Paper by Noboru Yamagata and Toshiko Yamagata (Bull. Chem. Soc. Japan, Vol. 31, No. 9, p. 1063, 1958).

Procedure

Sample Preparation

1. Urine - add 50 ml HNO_3 and 2 ml Cs carrier (CsCl-10 mg Cs/ml) to 500 ml urine in a beaker and evaporate to 50 ml. Transfer to a porcelain dish and heat to dryness. Moisten residue with HCl-HNO_3 mixture (1:1) and heat to dryness. Repeat treatment several times to destroy all organic matter. Extract dried residue with five 50 ml portions hot water and filter. Bring combined filtrate to approximately 300 ml and follow separation procedure.

2. Cereals, Vegetables, and Dry Milk - dry ash about 300-500 g cereals (100-200 g dried vegetables, 50 g dry milk) at 400°-450°C. Extract ash after addition of 2 ml Cs carrier with five 50 ml

portions hot HCl (1:10) and filter. Transfer combined filtrate to porcelain dish and evaporate to dryness after adding 50 ml HNO_3. Extract dried residue with five 50 ml portions hot water and filter. Bring combined filtrate to approximately 300 ml and follow separation procedure.

3. Soil (N-ammonium acetate extraction) - add 3 liters N-ammonium acetate solution (pH 7) to 300 g fresh soil in 5 liter beaker. Let stand 4-5 days with occasional agitation and filter. Add 2 ml Cs carrier and evaporate filtrate in porcelain dish to dryness. Moisten residue with HCl (1:1) and heat to dryness. Repeat several times to destroy all organic matter. Extract dried residue with five 50 ml portions hot water and filter. Bring combined filtrate to approximately 300 ml and follow separation procedure.

Separation

1. Add NH_4OH dropwise until dense precipitate of phosphates appears and add 2 ml excess. Allow to settle and test supernatant for complete precipitation by addition of NH_4OH. Filter and wash precipitate with NH_4OH (1:100). Combine filtrate and washings and discard precipitate.

2. Add 20 ml HNO_3 and 5 mg P (as H_3PO_4) and heat to 50-60°C. Add 20 ml 10% $(NH_4)_6 Mo_7O_{24} \cdot 4H_2O$, agitate vigorously, and rub wall with a glass rod to hasten precipitation. Let settle and cool. Filter and wash with 5 portions HNO_3 (2:100). Take up yellow precipitate with NH_4OH (1:1) and wash with water. Boil

combined filtrate and washings until odor of ammonia disappears. Dilute to 100 ml and cool.

3. Add 1 ml 10% $H_2PtCl_6 \cdot 6H_2O$ with stirring. Rub wall with glass rod until yellow precipitate appears. Let stand several hours. Filter through weighed one inch filter paper in Hirsch funnel and wash with 10 ml cold water and 3 portions ethyl alcohol. Dry at 110°C and weigh. Mount for counting. Standardize counter with known amount of Cs^{137} and 20 mg Cs carrier precipitated as chloroplatinate.

Notes

1. Overall yield of Cs is >85% and decontamination from other fission activities is $>10^5$ for Ce^{144} and Sr^{89}.
2. Contribution of Rb^{87} and K^{40} is negligibly small in the determination of Cs^{137} in biological materials by beta counting.

Procedure 8: Tetraphenylboron Extraction Method. Report by H. L. Finston, et al., Radiochemical Analytical Section, Brookhaven National Laboratory, Upton, N.Y.

Procedure

Step 1. Pipette an aliquot of the fission product solution ($\leq$ 5 ml) and 10 ml buffer solution (1 M $Na_3C_6H_5O_7$ in 0.5 M HNO_3 pH = 6) into a 125 ml separatory funnel. Adjust volume to 15 ml with H_2O.

Step 2. Add an equal volume of 0.05 M $Na\phi_4B$ in amyl acetate and extract the Cs activity into the organic phase by shaking for approximately 30 sec.

Step 3. Transfer aqueous phase to another separatory funnel and repeat Step 2. Combine organic phases in the first separatory funnel.

Step 4. Strip Cs activity from the amyl acetate phase by washing with two successive 10 ml portions 3 N HCl.

Step 5. Evaporate acid solution nearly to dryness and repeat Steps 1 through 4.

Step 6. Dilute aqueous phase to known volume and take suitable aliquots for counting in a γ-well scintillation counter (note 3).

Notes

1. Time for separation in duplicate is approximately 30 minutes.
2. Yield is 100% and decontamination factor from fission products is $\geqq 10^6$. Although procedure was developed for tracer solutions it has proved valid for solutions containing up to 10 mg Cs carrier.
3. The well counter is calibrated for efficiencies of Cs^{136} and Cs^{137} vs. a $4\pi\beta^-$ count. When the history of the sample is known (i.e. the irradiation and decay times) the relative amounts of each isotope are calculated.

Procedure 9: Thallium (I) Dipicrylaminate Precipitation Method. Paper on Carrier-free Separation of Cesium from Fission Products by the Use of Coprecipitation with Thallium (I) Dipicrylaminate by Noboru Yamagata and Sadakata Watanabe (Bull. of the Chem. Soc. of Japan 30, No. 6, p. 580, 1957).

Procedure

Step 1. Add 20 mg Fe ($Fe(NO_3)_3$ solution) and 5 mg Sr ($Sr(NO_3)_2$ solution) to the fission product solution (note 1). Make basic to thymol blue (pH 8-9) with NaOH solution, and add 1 ml 1M $NaCO_3$. Filter and was precipitate with water.

Step 2. Neutralize filtrate, if necessary, to pH 8-9, add 100% excess 3% sodium dipicrylaminate,[1] and cool for half hour in ice water. Add 1 ml 0.1 N $T1NO_3$ dropwise with constant stirring, and stir for 30 minutes at 0°C. Filter precipitate and wash with 2 ml ice water and with two 2 ml portions of diethyl ether at 0°C.

Step 3. Take precipitate up in 5-10 ml methylisobutyl ketone in a separatory funnel. Add 1 ml saturated chlorine water and 5-10 ml 2N HCl. Shake vigorously for 1 minute and transfer aqueous layer to another separatory funnel.

Step 4. Add an equal volume of methylisobutyl ketone to the aqueous layer. Shake vigorously for 1 minute. Evaporate aqueous layer to dryness in a small counting dish and count.

Notes

1. Sample must not contain K, NH_4, or Rb since they will be present in the final product as inert solids and are removed

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[1] E.B. Sandell, "Colorimetric Determination of Traces of Metals", Interscience Pub. Inc., N.Y. (1950), p. 501.

with difficulty. If U is present in the fission product sample, it must be previously removed by solvent extraction.

2. The recovery of active Cs is about 90% and the gross decontamination factor is $>10^4$, although the proposed procedure is valid only for about one year old fission products.

Procedure 10: Preparation of Carrier-free Cesium Tracer by Use of Ammonium Carrier. Paper 285 by L. E. Glendenin and C. M. Nelson, Nat. Nuclear Energy Ser., Div. IV, 9, Book 3, 1649-51 (1951).

Procedure

Step 1. Add 1 ml 1 M NH_4Cl and 5 ml 70% $HClO_4$ to the sample of fission material (note 1) in a 50 ml centrifuge tube. Evaporate by swirling over a burner until dense white $HClO_4$ fumes evolve (wear safety glasses). Caution: cool the solution under running tap water (note 2) and add 15 ml absolute ethanol; cool and stir for 1-2 minutes. Centrifuge and wash precipitate twice with 10 ml absolute ethanol.

Step 2. Take up precipitate in 10 ml H_2O, heat nearly to boiling, and add 5 mg Fe^{+++} carrier. Add 6 M NH_4OH dropwise with stirring, until $Fe(OH)_3$ precipitate coagulates (note 3). Centrifuge and discard precipitate. Add another 5 mg Fe^{+++} carrier, centrifuge, and discard precipitate.

Step 3. Evaporate supernatant solution to about 5 ml, add 4 ml 70% $HClO_4$, and evaporate to $HClO_4$ fumes by swirling over a burner.

Caution: cool under running tap water (note 2) and add 15 ml absolute ethanol. Wash precipitate twice with 10 ml absolute ethanol.

Step 4. Add 5 ml aqua regia to precipitate and evaporate to dryness.

Step 5. Repeat Step 4 twice.

Step 6. Take up carrier-free Cs activity in suitable volume of H_2O.

Notes

1. Original sample must not contain K or Na, since they will be present as inert solids in the final product.
2. Under the anhydrous conditions of the procedure, ethyl perchlorate is formed when ethanol is added to $HClO_4$. This compound is extremely explosive when heated. The solution must be kept cool during and after the addition of ethanol, and the supernatant solution should be discarded at once.
3. No more than 5 drops 6 M NH_4OH is usually required.
4. Final product is free of solids and is present in water solution with a small amount of $HClO_4$.

Procedure 11: Note on Preparation of Carrier-free Cesium Tracer. Paper 286 by R. Overstreet and L. Jacobson, Nat. Nuclear Energy Ser., Div. IV, 9, Book 3, 1652-3 (1951).

Procedure

Step 1. Digest an alkaline NH_2OH filtrate from a large sample of unseparated fission products containing about 5 g U, Sr^{89}, Ba^{140}, La^{140}, Cs^{137}, and traces of Ru^{106} and Te^{129} with aqua regia to destroy NH_2OH. Add 50 mg $CuCl_2$ and adjust acidity to 0.5 N HCl. Remove Cu and traces of Ru and Te as the sulfides.

Step 2. Bring filtrate to pH 2.5 and precipitate UO_4 with H_2O_2. Add Sr and Ba carriers and then remove with $(NH_4)_2CO_3$. Destroy the NH_4Cl in the filtrate with aqua regia.

Step 3. Evaporate residue and take up in 1 N $HC_2H_3O_2$. Add 50 mg NH_4Cl and sodium cobaltinitrite to precipitate the NH_4^+ and Cs^{137} tracer.

Step 4. Decompose precipitate in aqua regia and add Sr, Y, Zr, Ru, Te, Ba, La, Ce, and Th holdback carriers. Add 50 mg NH_4Cl and reprecipitate NH_4^+ with sodium cobaltinitrite.

Step 5. Decompose precipitate again and make a third precipitation without addition of holdback carriers.

Step 6. Decompose precipitate again and remove Co as CoS at pH 8-9.

Step 7. Evaporate filtrate, decompose NH_4Cl, and convert residue to the chloride. Adjust final solution to pH 2.6 to conform to other preparations.

Notes

1. Assay shows that the radioactive contamination of the cesium sample is <0.5% and that no detectable quantities of inert hold-back carriers are present.

Procedure 12: Preparation of Carrier-free 10 d Cs^{131} Tracer. Paper 287 by B. Finkle and W. E. Cohn, Nat. Nuclear Energy Ser., Div. IV, 9, Book 3, 1654-6, (1951).

Procedure

Step 1. Irradiate a quantity of ignited Baker's $BaCl_2 \cdot 2H_2O$. Six days after the end of the irradiation, dissolve the Ba salt in 3 N HCl and dilute to volume with H_2O.

Step 2. Precipitate $BaCO_3$ with $(NH_4)_2CO_3$ and dissolve in minimum amount 3 N HCl. Precipitate $BaCl_2 \cdot H_2O$ with conc. HCl.

Step 3. Dissolve in H_2O and reprecipitate $BaCl_2 \cdot H_2O$ three times.

Step 4. Dissolve $BaCl_2$, dilute with H_2O, and scavenge with Fe^{+++} precipitated with NH_4OH.

Step 5. Scavenge supernatant with $La(OH)_3$ and make two more $BaCl_2$ precipitations. This gives a clean Ba source.

Step 6. After several days milk Ba^{131} of its cesium daughter by dissolving $BaCl_2$ in H_2O and reprecipitate $BaCl_2 \cdot H_2O$ by dropwise addition of conc. HCl with vigorous stirring. Set precipitate aside for future Cs^{131} production.

Step 7. Clean supernatant solution of all Ba activity by five $BaCl_2$ precipitations, carried out by dropwise addition, with stirring, of 1 ml inactive Ba carrier (15 mg/ml).

Step 8. Boil supernatant solution to dryness, dissolve in H_2O, and scavenge twice with 5 mg $La(OH)_3$, with minimum amount of reagents.

Step 9. Evaporate tracer solution to dryness several times with aqua regia to remove ammonium salts, leaving solid-free 10.2 d Cs^{131} activity.

Notes

1. The product has high radiochemical purity, and the overall yield is about 30%.

Procedure 13: Paper Chromatographic Analysis of Irradiated Uranium in a Hydrofluoric Acid Medium.

Paper by C. E. Crouthamel and A. J. Fudge. J. Inorg. Nucl. Chem. 5, 240-244 (1958) and Quantitative Determination of Fission and Nuclear Reaction Products by C. E. Crouthamel, R. Heinrich, and C. Gatrouses, Talanta 1, 396-407 (1958).

Equipment

1. Papers used were 1/2" wide Whatman 3-MM, Whatman No. 1, or Whatman No. 2 paper strips. The papers were not pretreated.

2. Experiments were run in closed polythene cylinders with the paper centered at the top by a split cork stopper. At the bottom of the strip the paper was centered by a flat platinum spline inserted perpendicular to the plane of the paper before placing in the cylinder. When the paper was in position, the spline was below the developing solution surface, and the original sample spot was about 2.0 cm above the surface. The free volume of the polythene cylinders was relatively small: 29 mm diam. by 30 cm. With proper lighting, the solvent boundary was visible through the polythene. The atmosphere was saturated with solvent vapors by wetting the walls with the solvent just before introducing a strip into the vessel.

Procedure

Step 1. Dissolve irradiated uranium oxide with conc. HNO_3 containing about 1 µg Cs carrier per ml in a platinum crucible.

Step 2. Evaporate to dryness with a small amount of conc. HNO_3 under an infra-red lamp and dissolve in conc. HF.

Step 3. Convert nitrates to fluorides by two successive evaporations with conc. HF and dissolve residue in 1:3 HF.

Step 4. Place 2-100 µg uranium solution in a 5-10 mm circle on Whatman paper strips and air dry. Do not allow to spread to edge of the paper.

Step 5. Place paper strip in the polythene cylinder and develop with 60 g 49% HF per 100 ml dry $CH_3C_2H_5CO$. Chromatograms require 3-5 hours to develop.

Step 6. Cs isotopes were detected at center of chromatogram with a Geiger counter probe equipped with a defining slit over the window (note 1).

Step 7. Cut paper and mount between 25 mil mylar plastic and count with a scintillation spectrometer.

Step 8. Obtain absolute disintegration rate by comparing counting rate under 662 kev gamma peak of the sample and a $4\pi\beta^-$ calibrated Cs^{137} solution chromatographed in the same manner.

Notes

1. The yield of Cs by this analysis is 100%.
2. Method is not applicable to samples of very low burn-up values that require a large amount of fissile fuel.

Procedure 14: The Rapid Determination of Radioactivity Due to Cesium-137 in Mixed Fission Products by Anion Exchange and Gamma-Ray Spectrometry. Report by J. L. Woodhead, A. J. Fudge, and E. N. Jenkins, United Kingdom Atomic Energy Authority, AERE C/R 1877, Feb. 23, 1956.

Preparation of Resin - Dry normal grade Deacidite FF for 16 hours at 110°C. Grind in a coffee mill and grade into 80-100 mesh size. Make into a column, 12" x 1", by pouring into H_2O slowly and allowing to settle out. Pour 3 M Na_2CO_3 through the resin at about 10 ml/min until 10 column volumes (~250 ml) have passed through. Wash with twenty column volumes (~500 ml) of demineralized water. Pour resin into stoppered bottle and store under demineralized H_2O.

Procedure

Step 1. Slurry 1 g Deacidite FF (80-100 mesh), in the carbonate form, into a glass column, 25 cm x 0.7 cm diameter, fitted with a well ground tap and a fine tip. Use cotton wool plugs at top and bottom of the resin bed.

Step 2. Drain the water from the column until just above the top cotton wool pad (note 1).

Step 3. Take an aliquot of fission product solution and adjust its acidity to pH 1 by addition of alkali or by dilution with H_2O (note 2).

Step 4. Add 0.1 ml aliquots Cs (7.33 g $CsNO_3$/100 ml), Ru (note 3), Zr (3.0 g $ZrNO_3$ + 1.0 g $H_2C_2O_3$/100 ml) and Ba (1.9 g $Ba(NO_3)_2$/100 ml) carriers to the fission product solution and add 1 ml of the mixture to the resin column.

Step 5. Allow fission product solution to run into resin and collect eluant at about 6 drops/min (0.3 ml/min) in a small polythene cup. Wash column with 4 ml demineralized H_2O and collect in same cup.

Step 6. Stir the solution with a thin polythene rod. Stand the cup on a 250 mg/cm^2 Al absorber on the Al housing of a NaI(Tl) crystal of a gamma scintillation spectrometer.

Step 7. Determine the peak height of 5 ml of a $4\pi\beta^-$ counted Cs^{137} solution in a similar cup under identical geometry.

Notes

1. Care must be taken never to allow the column to run dry at any time during the procedure.
2. Salt concentration must not be greater than 3 M in the finally prepared sample.
3. Dissolve 2.04 g "specpure" $RuCl_3$ in an alkaline solution of KIO_4. Stir solution with an equal volume of CCl_4 and make acid with concentrated H_2SO_4. Wash CCl_4 phase once with water and treat with 30 ml 8 M HNO_3. Gas mixture with nitrous fumes from action of 8 M HNO_3 on Cu turnings until no more Ru is extracted. Boil HNO_3 solution to remove excess nitrous fumes, cool, and dilute to 100 ml with H_2O.

Procedure 15: Radiochemical and Mass Spectrometer Studies of Fission Product Cesium. Report by A. J. Moses and H. D. Cook, Analytical Chemistry in Nuclear Reactor Technology, Second Conference, Gatlinburg, Tennessee, TID-7568 (Pt.2), 192 (April 1959).

Modification of The Rapid Determination of Radioactivity Due to Cesium-137 in Mixed Fission Products by Anion Exchange and Gamma-Ray Spectrometry by J. L. Woodhead, A. J. Fudge, and E. N. Jenkins, United Kingdom Atomic Energy Authority, AERE C/R 1877, Feb. 23, 1956.

Procedure

Step 1. Add an aliquot of the mixed fission product solution to a Dowex-1 anion-exchange resin column in the carbonate form at a pH of about 6 (note 1).

Step 2. Cesium elutes in the first 3 ml. The column is then washed with 5 ml H_2O.

Step 3. Fume eluate to dryness with H_2SO_4, convert to chloride, apply to source filament of thermal emission mass spectrometer for isotopic analysis.

Notes

1. Resin serves as a solid precipitant for precipitating Zr, Nb, Ru and Ce.
2. Recovery of carrier-free Cs is nearly 100%; gamma spectrometry indicates pure Cs fraction.

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