Table III.	Effect	of Fluorid	e on	Colorimetric
D	etermin	ation of Si	lica	

(Fluoride complex	ed with Be ²⁺ ion)
SiO ₂ present, mg	SiO ₂ found, mg (5 mg fluoride added)
0.50	0.48
1.21	1.39
1.45	1.5
2.5	2.8
3.0	3.1

and large amounts of Th⁴⁺ a precipitate appeared on neutralization of acid solution). Ten milliliters of 10% ammonium molybdate was added. The solution was stirred, allowed to stand for 15 minutes and made to 250 ml in a volumetric flask, the absorbance was measured at 410 m μ . Fluoride does not interfere if sufficient amounts of Be²⁺ or Th⁴⁺ ions are present to complex the fluoride (Table III). Addition of borate is not necessary. Values of SiO₂ by the colorimetric method are included in Table I.

RESULTS AND DISCUSSION

Values of silica obtained by conventional method and by the described method (in presence of known amounts of fluoride) are tabulated in Tables I and II. Recoveries of 100 to 400 mg of SiO₂ in the presence of 50 to 200 mg of NaF are satisfactory. Small amounts of SiO₂ in presence of large amounts of fluoride have not been determined. For determination of such amounts Schrenk and Ode's procedure (7) might be more suitable. Large amounts of Be²⁺ ions hinder complete dehydration of silica. The method is expected to give satisfactory values for SiO₂ for most fluosilicates occurring in na-

ture such as amphiboles, topaz, micas, and phosphate rocks. Most of these are expected to contain less than 10% fluoride.

Fluorine must be determined in a separate portion of sample. The portion used for SiO_2 determination cannot be used for further analyses.

The following points have been noted. The ignited SiO_2 obtained by dehydration from a fused silicate or fused quartz was white powdery in appearance. While that obtained by dehydration of sodium silicate was found to be transparent-glassy solid especially when precipitated from solution containing Be²⁺ ions. The recoveries of SiO₂ from a sulfuric acid dehydration were short of being satisfactory. Casseroles and beakers may also be used for dehydration of SiO₂ in presence of fluorides provided fluoride is effectively complexed by Be²⁺, Th⁴⁺, or Zr⁴⁺ ions.

Inhalation of fumes, dusts, powders, mists, or solutions containing Be²⁺ must be avoided, since it is a hazardous material which may cause death or permanent injury after very short exposure to small quantities. Also, soluble compounds of beryllium may result in dermatitis. Frequent washing of hands etc., is necessary while working with beryllium-containing materials. Thorium and its compounds are radioactive. Storage of large amounts of thorium salts near the working shelf must be avoided.

The Al³⁺ method (8) may still be regarded as superior for the following reasons: nonpoisonous nature of Al³⁺, and recovery of SiO₂ is apparently greater.

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Precipitation of Berkelium(IV) lodate from Homogeneous Solution

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MANY PROCEDURES for separation and determination of metals have been improved by application of the technique of precipitation from homogeneous solution (PFHS), following methods initiated by H. H. Willard (I). An outstanding example is the Willard-Yu (2) method of precipitation of ceric iodate by formation of cerium(IV) ions from cerium(III) in a solution containing an excess of iodate ions.

Berkelium, still a very scarce element, has oxidationreduction properties very similar to those of cerium. Therefore, berkelium(III) in an iodate solution should be oxidizable to berkelium(IV) and precipitated similarly to cerium (IV), if the solubility of berkelium(IV) iodate is exceeded. When present in only tracer amounts, it should be coprecipitated with cerium. Thompson *et al.* (3) used cerium(IV) iodate to carry berkelium(IV) but apparently not from homogeneous solution.

The study reported here established a suitable procedure for coprecipitation of tracer-level berkelium with cerium,

Amer. Chem. Soc., 72, 2798 (1950).

compared the completeness of precipitation of these two elements, and measured the degree of contamination by several other elements, especially trivalent lanthanides and actinides. Information gained from this study indicates the future applicability of iodate PFHS to the recovery and purification of larger quantities of berkelium without the use of cerium carrier.

EXPERIMENTAL

Reagents. Cerous nitrate, nitric acid, iodic acid, sodium bromate, and small quantities of several other metallic salts were of analytical quality. Tracer ¹⁴⁴Ce and ¹⁵²Eu were obtained from the ORNL Isotopes Division and ²⁴⁹Bk and ²⁴⁴Cm from the transplutonium element production program.

Apparatus. The gamma activity of ¹⁴⁴Ce and ¹⁵²Eu samples was measured by a Nuclear-Chicago gamma spectrometer with a well-type NaI(Tl) detector. The beta activity of ²⁴⁸Bk and the alpha activity of ²⁴⁴Cm were measured by standard techniques in a Packard Tri-Carb Liquid Scintillation Spectrometer.

Procedure. A standard procedure was derived from results of preliminary tests and data of Willard and Yu. Bromate was chosen over persulfate as oxidizing agent because it gives more rapid precipitation. Chromate, useful as an

Louis Gordon, M. L. Salutsky, and H. H. Willard, "Precipitation from Homogeneous Solution," Wiley, New York, 1959.

⁽²⁾ H. H. Willard and S. T'Sai Yu, ANAL. CHEM., 25, 1754 (1953).
(3) S. G. Thompson, B. B. Cunningham, and G. T. Seaborg, J.

oxidant in extraction of berkelium as berkelium(IV) (4), is completely ineffective for ceric iodate precipitation. Addition of 1% CrO₃ to the bromate in the standard procedure greatly decreased ceric iodate precipitation and 5% CrO₃ prevented it. Consumption of the supply of berkelium was minimized by limitation of volumes to 10 ml. The usual quantities of reagents were HIO₃, 100 mg; NaBrO₃, 100 mg; $\hat{C}e$, 1 mg as $Ce(NO_3)_3$; and HNO_3 , 10 millimoles. The HNO₃ was varied in studies of its concentration effect. For convenience, salts and HNO₃ were added as solutions with 10 times their final concentrations. Tracers were used in separate series of experiments to facilitate accurate measurement of their activities. The cerium solution, quantitatively spiked from a standard and adjusted to prescribed conditions except for the bromate, was heated in a covered 30-ml beaker to 80-100 °C on a hot plate equipped with a magnetic stirrer. One half of the NaBrO3 was added and temperature and stirring were maintained for 10 minutes. The beaker was moved to an unheated stirrer and left for 30 minutes. The second half of the NaBrO₃ was then added and stirring continued for another 30 minutes. The contents of the beaker were transferred to a 15-ml centrifuge tube and spun in a clinical centrifuge.

For measurement of ¹⁴⁴Ce or ²⁴⁹Bk, the activity of a sample of the supernatant liquid was counted and compared with an equivalent sample of the standard spiking solution, thus determining the fraction not precipitated. There were possibly some positive errors in these measurements, because at the lowest acidities small but visible amounts of the precipitate floated on the solution.

Experience with this procedure indicated that the second addition of bromate is unnecessary but that about 1 hour is necessary to reach room temperature and maximum precipitation. No attempt was made to determine the necessary quantity of HIO₃. Preliminary separation of excessive amounts of salt or of interfering elements by such methods as solvent extraction, ion exchange, or alkaline precipitation will usually have preceded applications of the procedure. Conversion from chloride to nitrate is necessary before a second precipitation. Microtechniques with smaller volumes of solution should make the method applicable to very small amounts of berkelium (micrograms) without cerium carrier.

Removal of natural carrier cerium is unnecessary for determination of 249 Bk by liquid scintillation counting, but is necessary for obtaining the pure element. Apparently the best method for accomplishing this separation is one by Moore (5), which involves passing a solution of the two elements in 8N HNO₃ through an anion exchange column containing PbO₂. The berkelium passes through the column, while the cerium is quantitatively retained.

RESULTS AND DISCUSSION

Separation from Lanthanides and Actinides. The standard procedure was used to measure the thoroughness of precipitation of cerium and coprecipitation of berkelium, and the degree of contamination by europium and curium (Table I). The data indicate that the solubility of berkelium(IV) iodate is lower and less sensitive to acidity than that of cerium(IV). Contamination of ¹⁵²Eu was roughly inversely proportional to the concentration of HNO₃, reflecting the rather low solubilities of lanthanide triiodates. Most of the 1 mg of cerium in 10 ml of solution at HNO₃ concentrations less than 0.5N was precipitated by HIO₃ and then redissolved as the solution was heated. However, when 10 mg of natural europium was added to 1N HNO₃, the fraction of europium precipitated was only about half as high as with tracer ¹⁵²Eu alone. The added europium did not

Table I.	Effects	of Acidity	on Pred	cipita	tions of	Ce(l	V) and
Coprecipi	tation of	Bk(IV),	Eu(III),	and	Cm(III)	as	Iodates
from Homogeneous Solution							

HNO₃, <i>N</i>	Ce precipitated, %	Bk copre- cipitated, %	Eu carried, %	Cm carried, %
0.1	99.5	99.7	36	
0.2	99.7	99.6	15	
0.3	99.7	99.8	8.2	
0.4	99.8	99.8	4.4	
0.5	99.6	99.9	3.8	7.2
0.7	99.6	99. 7	3.6	
1.0	98.3	99.7	1.6	3.4
1.5	92.7	99.6	1.2	2.0
2.0	88.5	99.5	0.8	1.1
2.5	84.3	98.9	0.6	
3.0	35	91.9	0.4	

Table II. Behavior of Elements in Bk-Ce Iodate Precipitation

Behavior	Elements
Precipitated by HNO3 Precipitated by HIO3-HNO3 Precipitated by HIO3-HNO3- NaBrO3 Not precipitated	 Ti, Sn Zr, Ag, Hf, Th Mn, Bi, Pb Alkalies, alkaline earths, trivalent lanthanides, trivalent actinides, Al, Zn, Fe, Co, Ni, Cu, Cr, Mo, Hg, U

interfere with precipitation of cerium or berkelium. Contamination by curium was about twice that by europium. The data indicate that more than 99% of the berkelium can be recovered with removal of 99% of the trivalent lanthanides and actinides by a single precipitation from 2N HNO₃, though cerium precipitation is incomplete. An alternative is a double precipitation from 1N HNO₃. A decontamination factor of 800 from curium was obtained in this way when processing a mixture containing several metallic impurities.

Another alternative involves smaller amounts of cerium at lower acidities. With 0.1 mg of cerium in 1N HNO₃ only 0.2-0.4% of the europium or curium was carried, but losses of berkelium were 2-3%. However, 0.1 mg of cerium in 0.5N HNO₃ gave 99.2% coprecipitation of berkelium while carrying only 0.5% of the curium present. In most applications without cerium carrier, there will be only a few micrograms of berkelium, which should carry only very small amounts of trivalent actinides.

The crystalline ceric iodate precipitate is almost completely freed of included liquid by a single washing. Each further washing with 1% HNO₃ removes up to 0.1 as much cerium and up to 0.5 as much berkelium as was left in the original 0.1 *N* HNO₃, indicating some reduction of berkelium(IV).

Separation from Other Elements. The crystalline ceric iodate is not likely to carry other elements unless their iodates have low solubilities or they are precipitated in some other insoluble form. Thus the alkalies, though their nitrates may limit the reduction of process volumes, will not precipitate as iodates. Several other elements were tested by subjecting 1-mg quantities to the standard procedure in 1N HNO₃. Table II summarizes the behavior of these and some other elements. Of those which were precipitated at some stage in the process, only zirconium, from corrosion of process equipment, is likely to be present in nitrate process solutions. Its precipitation as iodate may carry some triva-

⁽⁴⁾ F. L. Moore, ANAL. CHEM., 38, 1872 (1966).

⁽⁵⁾ *Ibid.*, **39**, 1874 (1967).

lent actinides. It may be removed by extraction from 6NHNO₃ by a dialkylphosphoric acid without significant loss of berkelium. Some of the elements soluble as iodates in 1NHNO₃ would precipitate at lower acidities.

Applications. The primary application of iodate PFHS is in separating berkelium from other transplutonium elements after they have been separated from fission products and from plutonium. This appears especially attractive for final purification after process solutions have been reduced to small volumes.

Assay of radioactive solutions for their berkelium content is difficult because ²⁴⁹Bk has little activity except low-energy betas. Iodate PFHS gives high decontamination from interfering activities.

Another important application occurs as ²⁴⁹Bk decays with a half-life of 314 days to 249Cf. The californium may be recovered periodically as a solution after coprecipitating the berkelium with cerium. The precipitate can then be prepared for a later separation by dissolving in hydrochloric acid and converting to nitrate. Thus iodate PFHS is convenient for milking 249Cf from 249Bk. When sufficient ²⁴⁹Bk is available, this application can be made without cerium carrier.

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Indirect Spectrophotometric and Atomic Absorption Spectrometric Methods for **Determination of Perchlorate**

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RELATIVELY few spectrophotometric methods and no atomic absorption spectrometric methods for the determination of traces of perchlorate ion are found in the chemical literature. Methylene blue forms a very slightly soluble complex with perchlorate in aqueous solution. The methylene blue perchlorate complex can be extracted with chloroform (1) or 1.2-dichloroethane (2) and measured spectrophotometrically, or the excess methylene blue can be determined (3). Other dyes and extractants have been used in modification of this method (4, 5).

The decrease in color concomitant to the precipitation of copper(II) tetrapyridine perchlorate has been utilized in another indirect method (6). A redox reaction in which perchlorate was reduced to chloride by vanadium(III) to give an equivalent amount of vanadium(IV) was the basis of an indirect spectrophotometric method involving absorbance measurements at two wavelengths (7). The absorbance measurements at 400 and 750 mµ were necessary in order to correct for the absorbance due to the residual vanadium(III). A novel indirect spectrophotometric method has been proposed by Trautwein and Guyon (8). This method is based on the interference of the perchlorate ion in the development of the color due to rhenium-furildioxime complex formed when perrhenate is reduced with tin(II) chloride in the presence

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- (6) W. Bodenheimer and H. Weiler, ANAL. CHEM., 27, 1293 (1955).
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- (8) N. L. Trautwein and J. C. Guyon, ibid., 40, 639 (1968).

of α -furildioxime (9). The formation of an iron(II)-1,10phenanthroline-perchlorate complex extractable with nbutyronitrile (10) and the iron(II)-2,2'-bipyridine-perchlorate complex extractable with nitrobenzene (11) have been utilized as the basis of another indirect method for the spectrophotometric determination of perchlorate.

The spectrophotometric method proposed as the result of this investigation is based on (1) the formation of perchloratobis(2,9-dimethyl-1,10-phenanthroline) copper(I), (2) the extraction of this complex with ethyl acetate, and (3) measurement of the absorbance of the resulting extract (12). The atomic absorption spectrometric method involves aspiration of the extract into an acetylene-air flame and the copper determined using the resonance line of 3247 Å. A somewhat analogous approach has been suggested for the determination of nitrate (13).

EXPERIMENTAL

Apparatus. The atomic absorption spectrometric measurements were made with a Beckman Model 1301 atomic absorption accessory unit, a Beckman Model DB prism spectrophotometer equipped with a Beckman potentiometric recorder, and a Techtron burner assembly. The hollow cathode tube was neon filled and supplied by Beckman (No. 180245). The spectrophotometric measurements were made in 1.000-cm cells using a Cary 14 spectrophotometer. A Thomas shaking apparatus was used for extractions.

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