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PREPARATION AND CRYSTALLOGRAPHIC ANALYSIS OF CALIFORNIUM SESQUIOXIDE AND CALIFORNIUM OXYCHLORIDE

J. C. Copeland

(M. S. Thesis)

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ABSTRACT

This study was undertaken to extend the knowledge of the physical and chemical properties of californium. The preparation and crystallographic analysis of a low-temperature californium oxide of near-sesquioxide stoichiometry and of californium oxychloride have been carried out.

In an earlier study, 6 μg of Cf^{249} were purified. The purification techniques and analytical methods used for analysis of purity are summarized. Results of the purity evaluation indicated that the samples were adequately pure with respect to lanthanides and other actinides, but that impurities such as Ca or Al were potentially present. Because of the reasonably long half-life of Cf^{249}, the self-contamination of the sample since the time of purification was small.

Three samples of the low-temperature, cubic, Mn_2O_3-type californium "sesquioxide" were prepared. Two of these samples, prepared by the hydrolysis of other californium compounds, gave the same lattice parameters, within the error limits, with the average lattice parameter being $a = 10.838 \pm 0.02$ Å. The third sample, reacted in oxygen, had the lattice parameter $a = 10.809 \pm 0.003$ Å. In an earlier study, the lattice parameter of an air-ignited oxide sample was significantly smaller than the parameter of the same sample after heating in hydrogen. If these differences in lattice parameter reflect varying stoichiometries, then this might be evidence for higher and/or lower oxidation states of californium. The exact stoichiometries of the oxide samples prepared in this study are not known.

Three samples of californium oxychloride were prepared and were studied by x-ray diffraction techniques. The CfOCl had the tetragonal PbFCl-type structure and gave the average lattice parameters a = 3.956±0.002 Å and c = 6.662±0.009 Å.

The error limits reported for the lattice parameters of CfOCl and "Cf_2O_3" from the hydrolysis reactions are based on a statistical analysis of the consistency of the group of measurements. The limits placed on the lattice parameter of the "Cf_2O_3" sample from the reation with oxygen represent the 95% confidence level and reflect the internal consistency of the data for that particular sample.

I. INTRODUCTION

Californium, element 98, was first produced by the irradiation of Cm^{242} with 35-MeV helium ions

$$_{96}Cm^{242} + {}_{2}He^{4} \longrightarrow {}_{98}Cf^{245} + {}_{0}n^{1} \qquad (1)$$

Now microgram amounts of californium are produced during intensive neutron irradiation of Pu^{239}.[1] Isotopically pure Cf^{249} is obtained as the product of negative beta-particle decay of Bk^{249}.[2]

The availability of microgram amounts of californium makes investigation of some of the physical and chemical properties of this element possible. Some of the chemical properties of californium, especially its ion exchange behavior, were investigated in initial studies on separation and purification.[3] Some other studies of californium have included measurement of the magnetic moment of the +3 ion sorbed on cation exchange resin,[4] observation of the absorption spectrum of Cf^{+3} in a single crystal of anhydrous $CfCl_3$ and in a polystyrene-sulfonic acid matrix,[5] and the determination of the solution absorption spectrum.[6]

Microtechniques used in the preparation and identification of compounds of the actinides have been developed by B. B. Cunningham and J. C. Wallmann.[7,8] These techniques involve the absorption of the actinide isotope of interest onto a single bead of cation exchange resin. The organic matrix is removed during a high-temperature ignition so that only the oxide of the element remains. This compound may be transferred to a quartz capillary for further reaction and crystallographic investigation.

Preparation and analysis of the crystal structure of the Sm_2O_3-type californium sesquioxide and the UCl_3-type californium trichloride have recently been reported.[9] The present work reports the preparation and crystallographic analysis of Mn_2O_3-type californium sesquioxide and the PbFCl-type californium oxychloride. In the case of californium sesquioxide, the calculated lattice parameter varies with the method of preparation, indicating a possible variable stoichiometry. The "Cf_2O_3" and CfOCl lattice parameters are considered preliminary because of the possible stoichiometry problem in the oxide system and because of the questionable purity of materials used for both preparations.

II. Cf^{249} STARTING MATERIAL

A. Source of Cf^{249}

About 6 μg of Cf^{249} were collected and purified by J. L. Green in February 1965. A complete description of the purification techniques and analytical methods for evaluation of purity that were used has been given.[10] Part of this material absorbed on single beads of cation exchange resin, after storage for 2.3 years, was used for the compound preparation work of the present study. With the exception of Cf^{249} radioactive decay products, the purity evaluation made at the time of purification applies to the material used for the present study. Therefore, a summary of these results will follow.

B. Purification

The purification was carried out using standard ion exchange techniques. Initially, gross contaminants were removed by anion exchange columns, 2 M HCl cation clean-up columns, and alcoholic HCl columns. An α-hydroxyisobutyric acid column was used for separating out other actinides when they were present. The flow scheme used for the final purification is shown in Fig. 1. In the final purification processes, only high-purity reagents and specially-cleaned surfaces contacted the sample.

The purified Cf^{249} was absorbed onto specially purified Dowex cation exchange resin beads. The beads were commercially available Bio Rad Ag 50 × 4 cation resin washed with conductivity water, 1 M HCl, 6 M HCl and, finally, conductivity water. The ash content, determined to be 4.3 ppm, was considered to be a negligible contaminant as compared to the concentration of californium in the resin phase after saturation. A number of these "loaded" resin beads were used for the compound preparations in the present study.

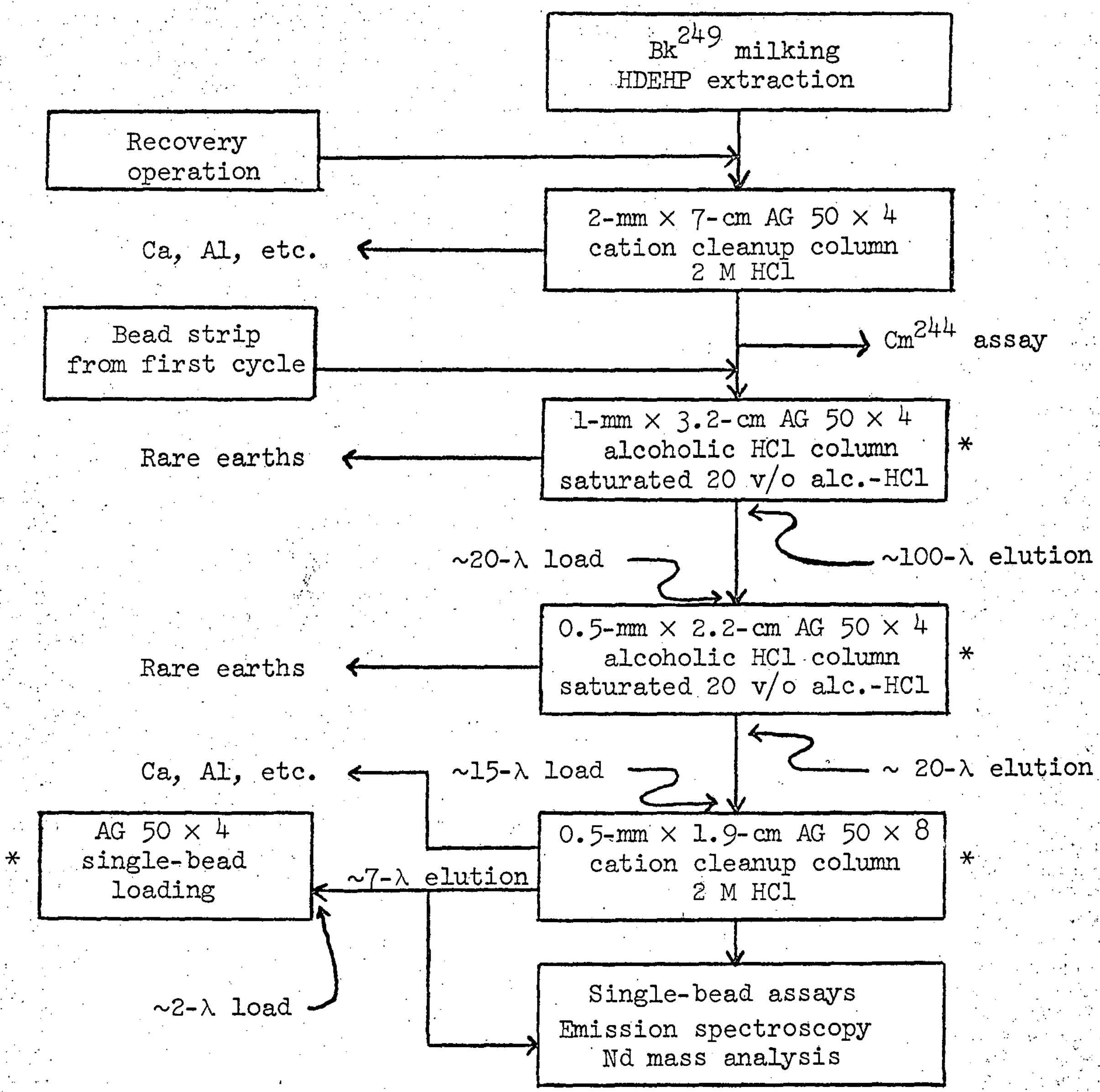

Fig. 1. Final purification cycle. The asterisk denotes high-purity operations carried out using leached quartz equipment and high-purity reagents (10).

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C. Analysis of Purity

Because a purity evaluation must be made from much smaller samples than those used in the purification processes, the danger of recontamination is great. The analytical data presented, therefore, should be considered as indications of upper limits of impurities in the sample.

1. Mass Analysis of Neodymium

Mass analysis for neodymium was carried out as an indication of total rare earth contamination. The conclusion of this analysis was based on the assumption that the rare earths were present in their natural abundances. This need not be a valid assumption but was considered adequate for this evaluation. The results showed 0.32 atom percent Nd. This indicates a total rare earth content estimate of 1.6 atom percent rare earths.

2. Analysis for Actinides

Standard alpha pulse-height counting techniques were used for the analyses of Pu, Am, and Cm. No peaks other than those of the californium isotopes were observed. Upper limits for Am and Cm content were calculated from the ratio of the number of counts in the Cf^{249} peak channel to the maximum scatter of counts in the energy ranges of the major peaks of the contaminating isotopes. Both Cm^{244} and Am content was set at less than one atom percent. It was not possible to set quantitative limits for the long-lived Pu^{242} isotope, but chemical and spectroscopic evidence seemed to indicate its absence.

3. Emission Spectroscopic Analysis

Emission spectroscopic analysis was carried out on about 150 ng of the purified Cf^{249}. The results are given in Table I. The only cation other than Cf detected was Be. With this one exception, the values listed are the limits of detection for the method used. The presence of 0.2 ng Be would correspond to contamination of about 3 atom percent. However, since the distribution coefficient for Be on Dowex 50 resin is smaller than for Cf, in a solution containing excess Cf, the bead should become saturated with Cf leaving most of the Be in the solution.

Table I. Results of emission spectroscopic analysis of the californium preparation in ng/150 ng Cf (10).

Ag < 10
Al < 10
Am < 100
As < 500
Au < 500
Be ∼ 0.2
Bi < 50
Ca < 10
Nb < 50
Cd < 500
Ce < 100
Cm ND
Co < 50
Cr < 10
Dy < 50
Er < 50
Eu < 10
Fe < 50
Ga < 10
Gd < 50
Ge < 50
Ho < 50
In < 50
Ir < 500
K < 5000
La < 10
Lu < 50
Mg < 10
Mn < 10
Mo < 10
Na < 5000
Nd < 100
Ni < 10
Np < 1000
Pa ND
Pb < 10
Pr < 500
Pu < 500
Re < 100
Rh < 50
Sb < 500
Sc < 10
Si < 10
Sm < 50
Sn < 100
Sr < 10
Ta < 500
Tb < 500
Th < 100
Ti < 50
Tl < 100
Tm < 50
U < 100
V < 10
W < 100
Yb < 10
Y < 10
Zn < 500
Zr < 10

4. Assay of Single Ion Exchange Bead

A single ion exchange bead assay was performed. This consisted of determining the total capacity of an ion exchange resin bead by saturation and elution of high-purity Am^{241}, followed by saturation and elution of the Cf solution. Both impurity cations and Cf would occupy the absorption sites in the resin. Therefore, assuming the same bead capacity as for the standard, the amount of impurities could be estimated. This type of evaluation can be particularly significant since it measures the Cf purity in the form in which it is used for compound preparation. The use of very small samples in this determination again requires that the results be considered as upper limits. Total impurities were determined to be about 0.35 eq/eq of Cf^{249}. Based on chemical and relative abundance considerations, the most probable contaminates were considered to be Ca and Al. X-ray studies did not, however, indicate gross contamination of the sample.

5. Calculation of Cm^{245} Contamination

Some of the Cf^{249} saturated resin beads from the above purification were carefully stored for 2.3 years before the present study. The only additional contamination of the californium samples during this time should be from the natural radioactive decay to Cm^{245}. Assuming a Cf^{249} half-life of 320±13 years,[11] contamination from this source would be 0.50 atom percent.

III. GLASSWARE AND EQUIPMENT

The quartz glassware used for making the x-ray capillaries was specially cleaned. It was first washed with soap and water, then boiled in ~6 M HCl, cooled, and allowed to stand for a few minutes. After rinsing with distilled water, it was boiled in distilled water. Following this, it was rinsed with conductivity water, then boiled in conductivity water. The glassware was then stored in quartz-distilled water until ready for use.

The compounds prepared in this study were examined by standard x-ray powder techniques. A model 80-000 Jarrel-Ash Microfocus x-ray source was used and was normally operated at 45 kV and 3.5 ma. Exposure times ranged from 11 to 22 hours. Ilford G Industrial film was used. Films were measured to a precision of 0.05 mm on a Norelco Film Reader made by Phillips Electronics, Inc.

The camera was a 57.3 mm diameter Norelco Precision Powder Camera, modified by Tom Parsons as shown in Fig. 2. The modifications permitted use of a type of x-ray sample capillary to be described later. The camera could be mounted in a vertical position as pictured, or in the normal horizontal position, so as to hold the sample capillary in either a vertical or horizontal position. The changes in camera design prevented full rotation of the sample; oscillation through about 100 degrees was used. This oscillation was sufficient for the polycrystalline compounds examined.

CuK_α radiation was used, CuK_β being removed by a 0.00035-inch nickel foil filter inside the x-ray camera. This filter also served to minimize the exposure of the film to the radiation given off by the sample.

IV. COMPOUND PREPARATION

The starting point for the preparation of a variety of californium compounds is the air ignition of a single bead of sulfonic acid resin saturated with Cf^{+3}. Beads of about 0.09 mm in diameter with a capacity of approximately 200 ng of californium were used. The apparatus used for the ignition is shown in Fig. 3. The bead is transferred to the 0.005-inch platinum wire with a fine quartz fiber. The surface of the wire may be lightly coated with glycerine to help insure that the bead is initially held in place and positioned correctly. As the platinum rod is gradually heated with a microtorch, the bead goes through distinct changes. The 2.3-year-old californium beads were black because of partial self-ignition due to the radiation of the californium, although freshly-loaded beads are normally light yellow. If the bead is not

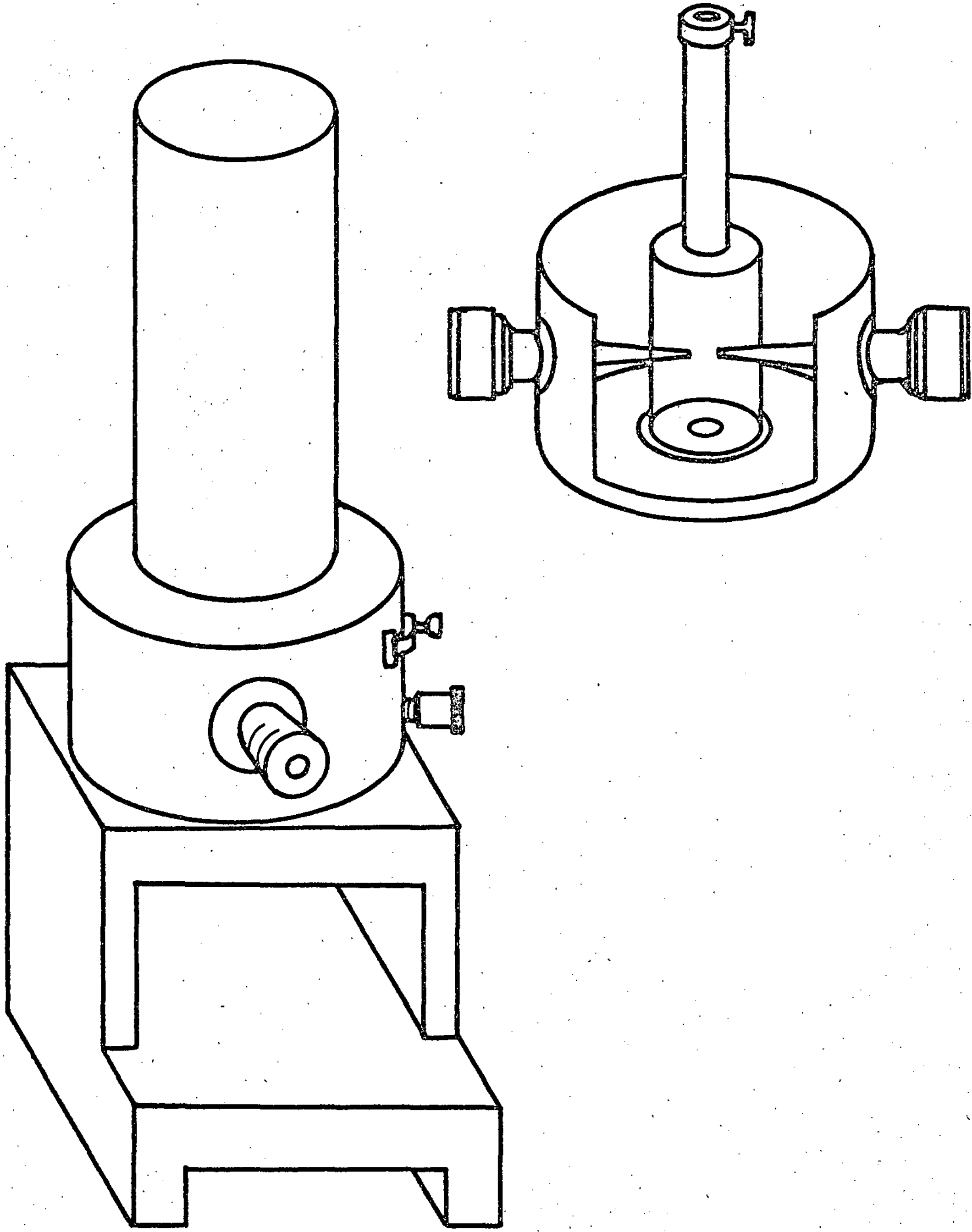

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Fig. 2. Modified X-Ray Camera.

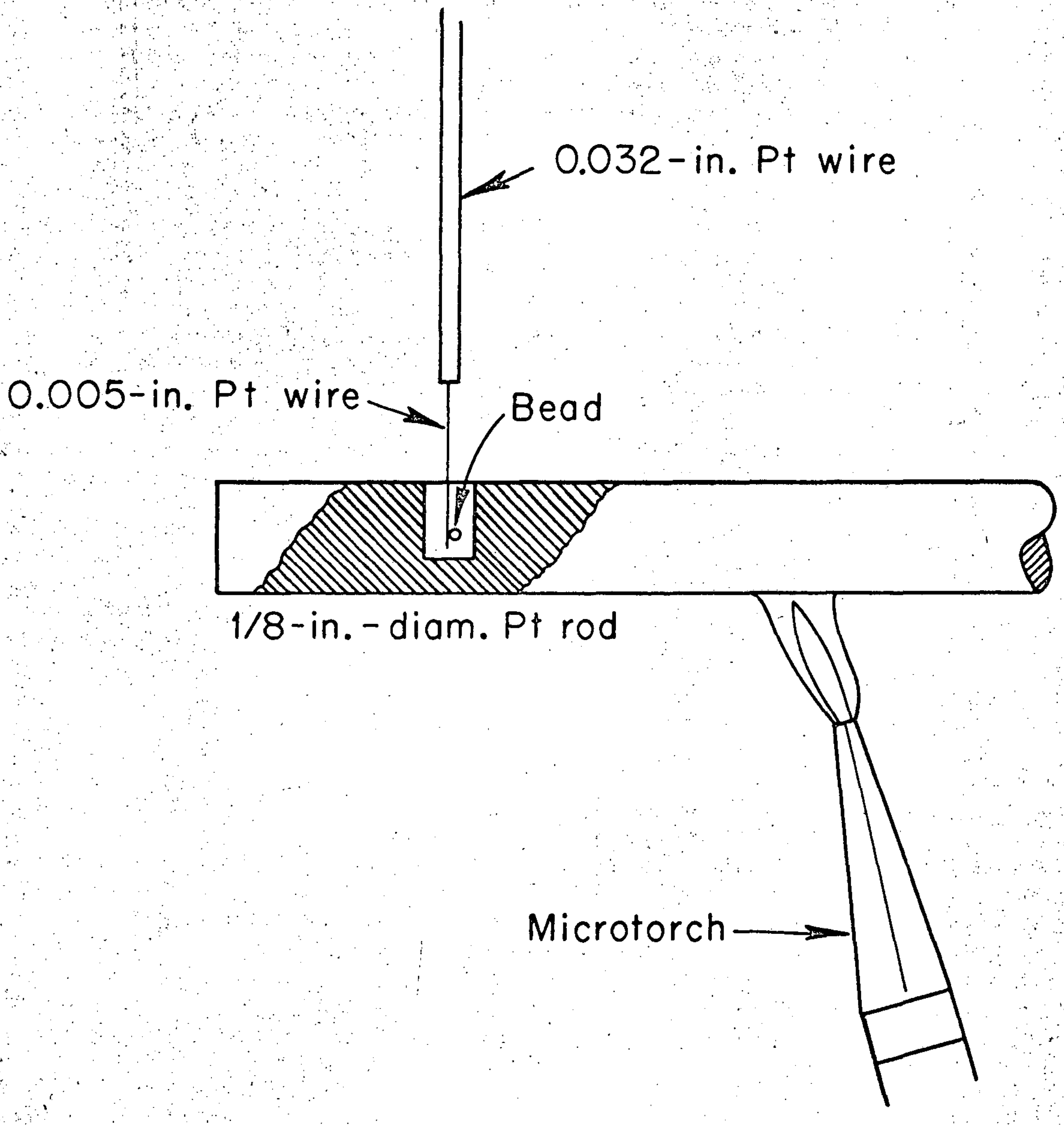

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Fig. 3. Bead-Ignition Apparatus (10).

already black, the initial stages of the heating quickly cause the bead to darken. Then, as the temperature is raised to about 600° C, the organic material burns off, the californium becomes a light-colored "sulfate," and the bead of material shrinks to approximately one-half its original diameter. Until this shrinkage occurs, heating must be done slowly so that a quick volume change will not cause the bead to explode. The "sulfate" may then be heated more quickly up to about 1150-1200° C to convert the californium to the air-stable oxide.[12] An optical pyrometer was used to measure the temperature of the rod around the sample as an indication of the temperature at which the reaction was taking place, although the actual temperature of the sample under these conditions is not known. The bead is then dislodged as shown in Fig. 4 and falls into a thin-walled quartz capillary drawn on the end of a standard taper that has been specially cleaned.

The capillaries were designed so that an approximately 200 ng californium sample with an ignited diameter of about 0.045 mm would lodge about 2 mm above the sealed capillary tip. The capillary wall thickness was kept to 1/10 to 1/5 the inside diameter of the capillary to avoid extensive background scattering of x-rays in the x-ray powder patterns of the sample.

The air-ignited oxide may be reacted on a preparation vacuum line before a diffraction pattern is taken, or the oxide itself may be made ready for a diffraction pattern. Before a diffraction pattern is taken, the capillary is evacuated to about 10^{-6} mm Hg and sealed off. Previously, this seal was accomplished by melting the capillary above the sample with a flame as is shown in Fig. 5a and removing this section from the standard taper. The sample then could be mounted in a standard x-ray powder camera for a diffraction pattern. This capillary section containing the sample could later be cracked open, resealed to its standard taper with Apiezon W wax, reacted to give another compound, and again sealed off.

In this study, however, the capillary tip was pulled on a taper that was part of a twist stop-cock as is shown in Fig. 5b. After the capillary was evacuated, it was sealed by simply closing the stop-cock.

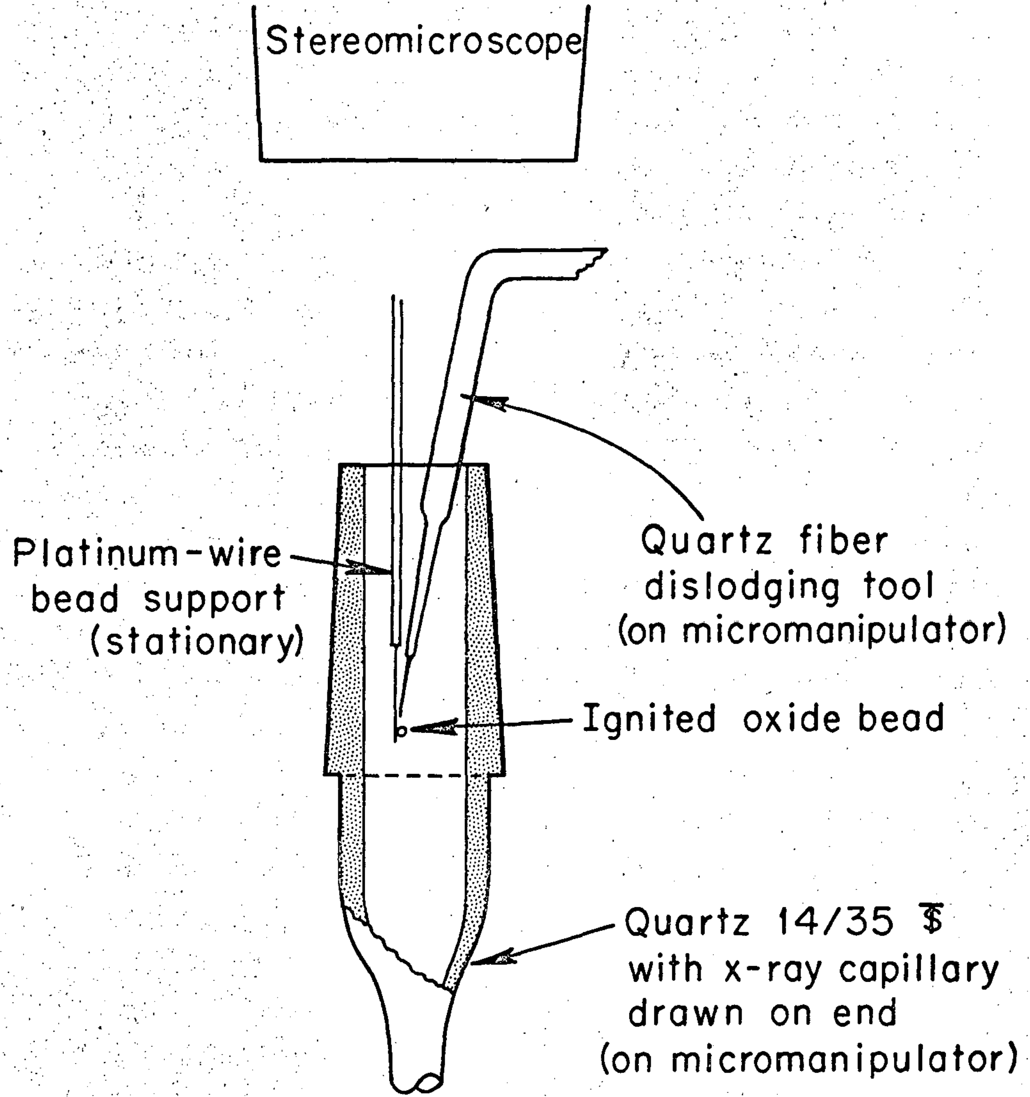

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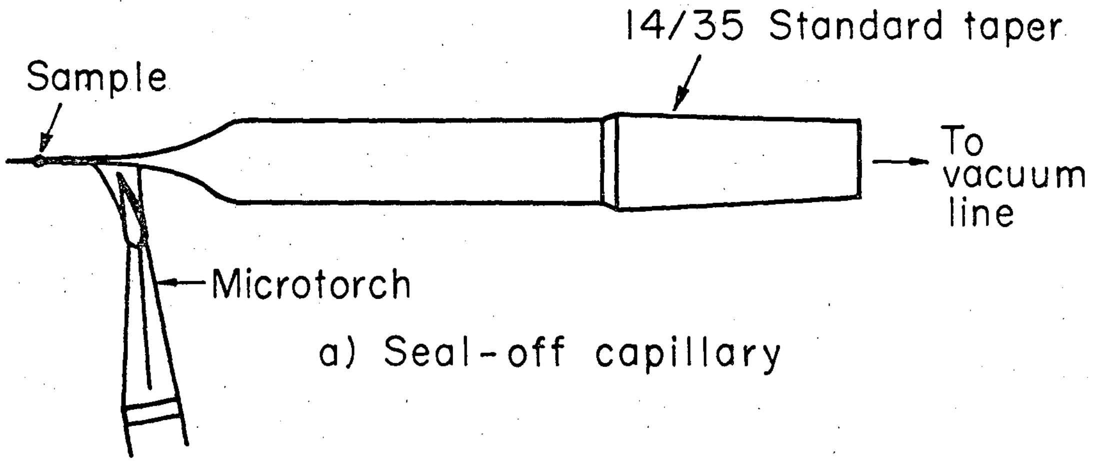
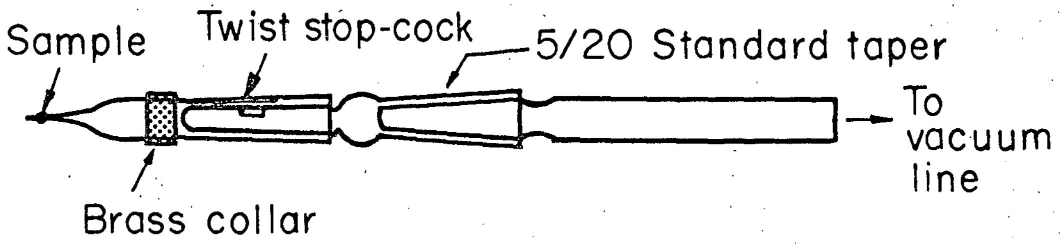
Fig. 4. Apparatus For Transferring Ignited Oxide Bead to X-Ray Capillary (10).



a) Seal-off capillary



b) Stop-cock capillary

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Fig. 5. Capillaries.

The obvious advantages of this capillary over the seal-off capillary are 1) fewer manipulations of the sample between reactions reduces the chance of breakage or loss of the sample and 2) the number of times a sample may be reacted is unlimited. This type of capillary was found suitable for the preparation of air-stable compounds. However, attempts to maintain anhydrous conditions, as in the preparation of $CfCl_3$, were unsuccessful. This suggests that enough water to hydrate a very small hygroscopic sample can come from the exposed walls of the stop-cock capillary. In the seal-off capillary the wall surface area is small and does not yield enough water to hydrate the sample. The inability to maintain anhydrous conditions is a definite disadvantage of the stop-cock capillary.

A. Preparation of "Cf_2O_3"

Three individual californium samples were used in the preparation of the low-temperature oxide. Because these samples were used in a series of reactions, the californium compound that served as the starting material for the preparation of "Cf_2O_3" varied from sample to sample. Table II summarizes the method of preparation used for each oxide sample.

Fig. 6a shows schematically the vacuum line and other apparatus used for the preparative work. For the preparation of the oxide by hydrolysis, the attachment shown in Fig. 6b was connected to the gas inlet of the preparation vacuum line. High-purity nitrogen gas acting as a carrier was bubbled through bubbler 2 which contained conductivity water. The spray trap was included to insure that no liquid droplets reached the sample. The reactions were carried out under flow conditions to facilitate removal of gaseous reaction products. The flow rate could be monitored at bubbler 1.

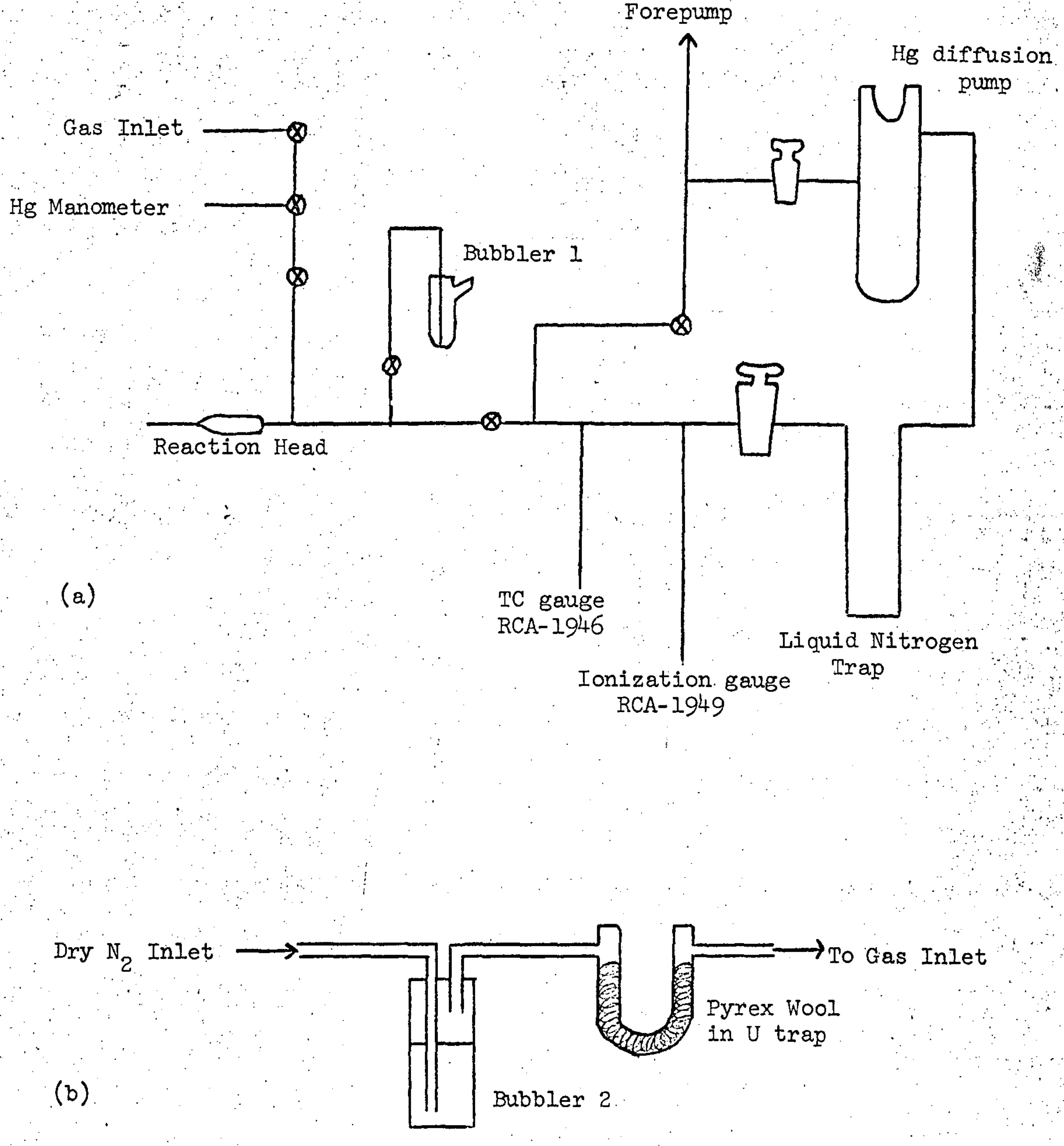
In general, the directions for preparation of "Cf_2O_3" by hydrolysis are: react californium compound with water vapor at 500-600° C for 15-20 min.

One californium oxide sample was also obtained by reaction of californium oxychloride with oxygen. The steps in the reaction were:

Table II. Summary of preparation of "Cf_2O_3".

Sample	Method of Preparation	Appearance
JC-II	CfOF + H_2O(g)(N_2(g) carrier) for 20 min at 614-638°C	Not observed under magnification
JC-III	CfOCl + H_2O(g)(N_2(g) carrier) for 15 min at 500-545°C plus 15 min at 600°C in vacuum	light color (green?)
JC-IV	CfOCl + O_2(g)(1/2 atm) for 23 min at 730°C Not under anhydrous conditions	"dark" in color

Fig. 6. Preparation Vacuum Line.



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1) Sample was vented to 1/2 atm. O_2.
2) Sample was heated for 10 min at 730° C.
3) Capillary was evacuated to about 40 microns.
4) Sample was again vented to 1/2 atm O_2.
5) Sample was heated 13 min at 730° C.
6) Capillary was evacuated to 2×10^{-5} mm Hg and closed off.

The sample was not necessarily reacted with "dry" O_2 because of the stop-cock capillary used. Nevertheless, the reaction took place in an oxidizing atmosphere.

B. Preparation of CfOCl

The probable reactions for the formation of the californium oxychloride are summarized in Table III. A compound that was assumed to be hydrated $CfCl_3$ was the result of attempts to prepare anhydrous $CfCl_3$. But, as has already been discussed, the stop-cock capillary used did not maintain anhydrous conditions. Heating this compound resulted in the formation of the californium oxychloride.

The reaction of the oxide with HCl-H_2O vapor mixture is perhaps a more satisfactory technique for the preparation of the oxychloride. For this reaction, the attachment shown in Fig. 6b was connected to the gas inlet on the preparation vacuum line. Bubbler 2 contained 12 M HCl, a concentration that gives the correct HCl(g) and H_2O(g) partial pressures to produce AmOCl from $AmCl_3$.[13] The oxide was reacted with the vapor for 20 min at 505° C.

Table III. Summary of preparation of CfOCl

Sample	Method of Preparation	Appearance
JC-II	Cf_2O_3 + HCl-H_2O mixture for 20 min at 505°C	green color
JC-III	$CfCl_3 \cdot XH_2O$ in the presence of 1/2 atm H_2 for 20 min at 555-585°C	not observed under magnification
JC-IV	$CfCl_3 \cdot XH_2O$ heated in vacuum for 10 min at 450°C	medium green color

V. CRYSTALLOGRAPHIC ANALYSIS

X-ray powder patterns were taken of the "Cf_2O_3" and CfOCl samples. Fig. 7 shows representative films of the two compounds. All the oxide samples prepared gave broad, high-angle lines, while the oxychlorides were sharp to $2\theta = \sim 163°$. The oxide pattern in Fig. 7 required a 22 1/2 hour exposure time, while the oxychloride was only exposed 11 1/2 hours. The oxide sample was still a spherical bead; the oxychloride had been melted in earlier reactions and was crystallized on the walls of the capillary over about a 1 mm distance. The examples in Fig. 7 demonstrate the film quality that can be obtained with these very small 200 ng, radioactive samples.

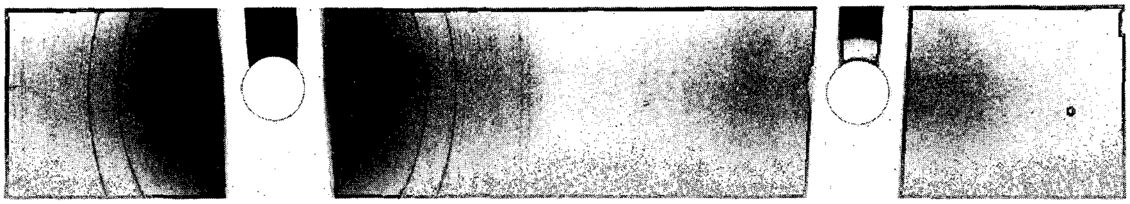
All films except Film 2904A were measured by two independent observers and their 2θ data averaged. The observed lines were indexed by comparison to data of isomorphic compounds. The intensities of observed lines were compared to the theoretical intensities calculated by the POWD computer program developed by D. K. Smith.[14] The most probable lattice parameters were calculated by a least squares fit of the differences in observed and calculated line positions using the LCR-2 computer program of D. E. Williams.[15] The weight given to each line in the fit is given by

$$W_i = \frac{\text{constant}}{\sin^2 \theta_i \, (\Delta\theta_i)^2} \qquad (2)$$

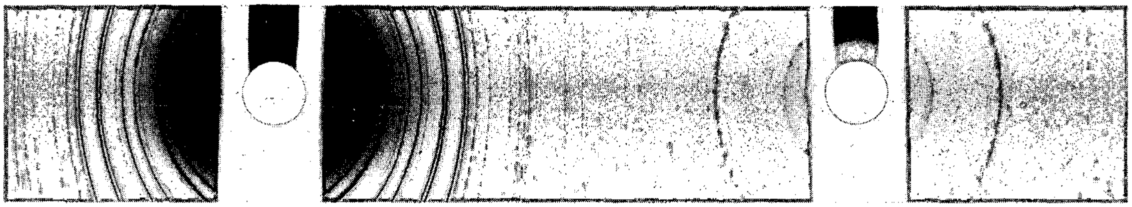
where $\Delta\theta$ is the estimated standard deviation of θ. In analysis of the films, $\Delta\theta$ was taken as 0.05 degrees, the precision to which a line position could be estimated, excepted when two or more lines fell so near each other that they were visually observed as one line. In this case, a $\Delta\theta$ given by

$$\Delta\theta_i = \Delta\theta_g \sqrt{\frac{I_i + I_j + I_k + \cdots}{I_i}} \qquad (3)$$

was assigned to each line in the group so that the $\Delta\theta_g$ of the group remained 0.05 degrees. No extrapolation functions were used since use of precision cameras and small samples essentially eliminates errors due to absorption and eccentricity.



a) "Cf_2O_3" - Mn_2O_3-type cubic sesquioxide. Film 2902A. Sample JC-II.



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b) CfOCl - PbFCl-type tetragonal oxychloride. Film 2736A. Sample JC-III.

Fig. 7. X-ray Powder Patterns of "Cf_2O_3" and CfOCl.

Error limits placed on the lattice parameters calculated by the LCR-2 computer program from the averaged data of two independent observers represent the 95% confidence level and reflect the internal consistency of the data for that particular sample. Another possibility for the assignment of error limits exists. If the data are treated statistically, the resulting error limits reflect the probability that independent samples and techniques will give a lattice parameter within the error limit range. This is probably more valuable information than the internal consistency of data for individual preparations.

Standard deviations can be calculated by

$$\sigma = \frac{t}{\sqrt{N}}\sqrt{\frac{\Sigma(d_i)^2}{N-1}} \qquad (4)$$

The σ is the error limit for a particular confidence level for N independent measurements. The d_i are the absolute deviations from the average of the set of measurements. The Student t value, t, takes into account the effect of using only a few measurements. For the 95% confidence level, t equals 4.30 for three measurements and 12.71 for two measurements. For two or three measurements, then, the error limits are ordinarily larger than those set from consideration of internal consistency only. The error limits set on the averaged lattice parameters of the individual preparations in this work are the 95% confidence level based on statistical analysis and, therefore, are a more conservative estimate than is ordinarily reported. Variation of the lattice parameters outside these limits could indicate nonstoichiometry, impurities in the sample, radiation damage to the lattice, and the like.

A. Californium "Sesquioxide" Results and Discussion

Three individual low-temperature oxides were prepared and x-ray powder data were recorded and analyzed. The oxides exhibited the Mn_2O_3-type, bixbyite structure. Table IV presents the calculated lattice parameters for the three oxide samples whose preparation has been described. In earlier work,[16] two reactions of a californium sample resulted in the formation of californium oxides. This earlier sample, however, may have

Table IV. Crystal data for "Cf_2O_3".

Sample	Film	Observed		Method of Preparation
		a(Å)[a]	2σ[b]	
JC-IV	2785A	10.809	0.003	Reaction of CfOCl in O_2(g)
JC-II	2902A	10.839	0.005	Hydrolysis of CfOF
JC-III	2896A	10.836	0.006	Hydrolysis of CfOCl
	JC-II + JC-III Average		10.838 ± 0.02Å[c]	

[a] Calculated by LCR-2 computer program

[b] Represents the 95% confidence range and reflects the internal consistency of the data for a particular sample.

[c] Calculated using

$$95\% \text{ confidence limits} = \frac{t}{\sqrt{N}}\sqrt{\frac{\Sigma(d_i)^2}{N-1}}$$

contained as much as 8.1 atom percent rare earths. The sample was first air ignited and was found to exhibit the Mn_2O_3-type cubic structure (Film 2230A). After reduction of the sample in $H_2(g)$ for one hour at 610° C (Film 2423A), the structure was still the Mn_2O_3-type, but the lattice parameter had increased by 0.49%. This air-ignited sample and sample JC-IV reacted in $O_2(g)$ gave essentially the same lattice parameter. The similarity in parameter may be coincidental since the purity of the two samples with respect to rare earth content is believed to differ significantly. This parameter obtained from the samples reacted under oxidizing conditions is substantially lower than the parameter obtained for the oxide sample produced by a hydrolysis reaction. Further, the air-ignited sample that was then annealed in a reducing atmosphere gave a parameter higher than the parameter of the hydrolyzed sample. But the purity of this "reduced" sample makes the results obtained questionable. These differences in lattice parameters are greater than the error limits set on the averaged lattice parameter of the hydrolyzed samples based on a statistical analysis.

The most obvious explanation for the above variation in lattice parameter would seem to be a variable stoichiometry. The scale of operation essentially eliminates direct analysis of composition. Any assignment of stoichiometry must come from analogy with other compounds.

Some work has been done on the nonstoichiometric oxides of praseodymium,[17] terbium,[18] and americium[19] in the composition range between a sesquioxide and a dioxide. In these rare earths, the compounds with compositions approaching those of a dioxide exhibited a face-centered cubic lattice. Crystal structures other than cubic appeared for compounds in the intermediate composition range. For compositions near that of a sesquioxide, a body-centered cubic lattice was evident, and the lattice parameter increased as the composition approached that of a stoichiometric sesquioxide. In the gadolinium, erbium, and lutetium oxide systems, samples with oxygen to metal ratios ranging from 1.495 to 1.485 were examined and were found to have essentially the same cubic lattice parameter as their stoichiometric sesquioxies.[20]

The stoichiometries of the californium oxides prepared are not known. However, two oxide samples prepared by hydrolysis had the same lattice parameter within experimental error. This, at least, indicates a composition of some stability. If these samples produced by hydrolysis are assumed to be stoichiometric Cf_2O_3, then the crystallographic data would seem to indicate a tendency toward a higher and possibly a lower oxidation state. The affect of H_2(g) and O_2(g) on the lattice parameter of the oxide prepared by hydrolysis is presently under further investigation.

All of the actinides through berkelium are known to have multiple oxidation states, while californium is only known to exist in the +3 state.[21] Dysprosium, the chemical homologue of californium, is only known to have a +3 oxidation state. It is possible, however, that Cf^{+5} compounds might exist because of stability of $5f^7$ configuration. Yet, repeated attempts to oxidize Cf^{+3} to a higher oxidation state have been unsuccessful.[22] The crystallographic data presented for "Cf_2O_3" could represent an observation of an oxidation state higher than the +3 state in californium.

The possibility of stability of a lower oxidation state may exist. There is an increasing stability of lower oxidation states, particularly the +3 state, in going up the actinide series of elements.[21] The preparation of AmO has been reported.[23] The preferential extraction of californium in sodium amalgam and its preferential electrolytic separation suggest the possibility of a +2 state of californium.[24] Attempts to prepare a pure Cf^{+2} compound have resulted in a change of phase of $CfCl_3$ in the presence of H_2 from the hexagonal $CfCl_3$ to an as yet unidentified phase.[25] It is possible that the oxide crystallographic data could reflect the presence of a +2 oxidation state of californium.

The stoichiometry of the oxides prepared cannot be assigned, but the observation of what appears to be a variable stoichiometry is in itself valuable information. Because of the question of stoichiometry and of purity of the sample used, it is felt that the "Cf_2O_3" lattice parameters reported should be considered preliminary.

Table V gives a list of theoretical and observed line positions and intensities for a "Cf_2O_3" sample prepared by hydrolysis. All lines that are theoretically present through $2\theta = 144.89$ degrees were seen except for the low-intensity lines 200, 420, 422, 752, 664, 1011, 880,

Table V. Line list and indexing for cubic californium sesquioxide - Film 2902A, JC-II.

	2θ		Intensity	
hkl	calculated[a]	observed[b]	calculated[c]	observed[d]
211	20.07	20.07	0.83	1.5
222	28.53	28.53	10.00	10.0
321	30.87	31.00	0.25	< 1.0
400	33.06	33.03	3.99	8.5
411	35.13	35.13	0.53	2.5
332	38.97	39.03	0.23	< 1.0
431	42.53	42.63	0.73	4.0
521	45.85	45.90	0.17	< 1.0
440	47.45	47.43	3.85	8.0
433	49.00	49.03	0.22	< 1.0
442	50.52	50.48	0.04	< 1.0
611	52.01	52.03	0.46	1.5
620	53.46	53.46	0.10	1.0
541	54.89	55.03	0.36	1.5
622	56.30	56.33	3.54	7.5
631	57.68	57.78	0.57	1.5
444	59.04	59.08	0.81	3.5
543	60.39	60.53	0.24	1.0
640	61.71	61.63	0.11	< 1.0
721	63.02	62.98	0.29	1.0
642	64.31	64.33	0.14	< 1.0
651	68.11	68.14	0.32	1.5
800	69.36	69.39	0.49	2.0
741	70.59	70.49	0.41	1.0
644	71.82	71.84	0.20	< 1.0
653	73.03	72.94	0.24	< 1.0
822	74.24	74.29	0.13	< 1.0

Table V (continued)

	2θ		Intensity	
hkl	calculated[a]	observed[b]	calculated[c]	observed[d]
831	75.44	75.49	0.41	1.5
662	76.64	76.69	1.07	4.0
840	79.01	79.04	0.86	3.5
833	80.19	80.14	0.13	< 1.0
842	81.36	81.34	0.11	< 1.0
921	82.53	82.59	0.29	1.0
851	84.87	84.94	0.31	1.0
763	87.19	87.29	0.24	< 1.0
844	88.35	88.44	0.74	3.0
941	89.51	89.49	0.30	< 1.0
$1000\alpha_1$	90.57	90.79	0.11	< 1.0
$862\alpha_1$	92.89	92.94	0.24	1.5
$943\alpha_1$	94.05	94.08	0.06	< 1.0
$666\alpha_1$	95.21	95.29	0.50	3.0
$765\alpha_1$	96.38	96.49	0.24	< 1.0
$774\alpha_1$	98.71	98.79	0.21	1.5
$864\alpha_1$	99.88	99.68	0.20	< 1.0
$1033\alpha_1$	101.06	100.99	0.16	< 1.0
$1042\alpha_1$	102.24	102.28	0.19	< 1.0
$873\alpha_1$	103.43	103.84	0.17	< 1.0
$963\alpha_1$	105.82	105.79	0.21	1.0
$1053\alpha_1$	110.70	110.49	0.19	< 1.0
$1062\alpha_1$	114.46	114.70	0.50	2.5
$1200\alpha_1$	117.03	117.70	0.26	1.0 broad
$1211\alpha_1$	118.34		0.19	
$1220\alpha_1$	119.66	120.90	0.17	1.0 broad
$1071\alpha_1$	121.00		0.20	
$1222\alpha_1$	122.36		0.25	

Table V (continued)

	2θ		Intensity	
hkl	calculated[a]	observed[b]	calculated[c]	observed[d]
983_{α_1}	123.74	123.55	0.20	1.0 broad
1073_{α_1}	126.57	126.40	0.24	< 1.0
1240_{α_1}	128.03	128.30	0.34	< 1.0
1242_{α_1}	131.03	130.85	0.49	< 1.0 broad
1084_{α_1}	144.89	144.75	0.74	< 1.0 broad

[a] Calculated using a = 10.839 Å, CuKα (λ = 1.54178 Å), CuKα_1 (λ = 1.54051 Å), CuKα_2 (λ = 1.54433 Å).

[b] Averaged readings of two independent observers.

[c] Calculated using the POWD intensity program assuming the atomic coordinates of $(Fe,Mn)_2O_3$. Calculation is scaled so that the strongest line has an intensity of 10.0.

[d] Averaged readings of two independent observers estimated visually on a scale from 10 to 1.

1044, 866, 875, 965, 1233, 976, 1082, 985, 1066, 1075, and 994. A minor platinum metal phase was present and could be indexed satisfactorily. Since the original air ignition of the sample was carried out on a platinum wire, the presence of the platinum phase is not unexpected. Three other lines not indexed as platinum metal or as "Cf_2O_3" were observed at $2\theta = 25.83$, 27.98 and 32.43 degrees. The intensity of these lines was estimated visually as 1 based on a scale from 10 to 1.

Fig. 8 shows a plot of the lanthanide and actinide cubic lattice parameters. The effect of the half-filled f shells is shown by the cusp in going from Gd to Tb in the lanthanides and more pronouncedly in going from Cm to Bk in the actinides. The two oxide parameters for californium calculated in this work are plotted.

B. Californium Oxychloride Results and Discussion

Powder diffraction patterns of the oxychloride samples described were taken and analyzed. Californium oxychloride exhibits the tetragonal PbFCl-type structure. The calculated lattice parameters are given in Table VI. No deviation from stoichiometry was indicated. The lattice parameters should be regarded with caution because of the question of purity of the sample.

Table VII gives a comparison of theoretical and observed line positions and intensities for a representative CfOCl sample. All theoretically present lines through $2\theta = 163.14$ degrees were observed with the exception of the 001 which was off the measureable part of the film and the low-intensity lines 006, 323, 007, 331, 117, 413, 207, 404, 306, 008, 334, and 227. A minor platinum phase was present and was indexed. Two lines not indexed as platinum metal or californium oxychloride were observed at $2\theta = 23.61$ and 28.86 degrees. Their intensity was estimated visually as about 2 on a scale from 10 to 1.

Figs. 9 and 10 show plots of the a and c lattice parameters of the tetragonal lanthanide and actinide oxycholorides that have been prepared. The lattice parameters plotted for berkelium are from a

Fig. 8. Lattice Parameters of Lanthanide and Actinide Cubic Sesquioxides.

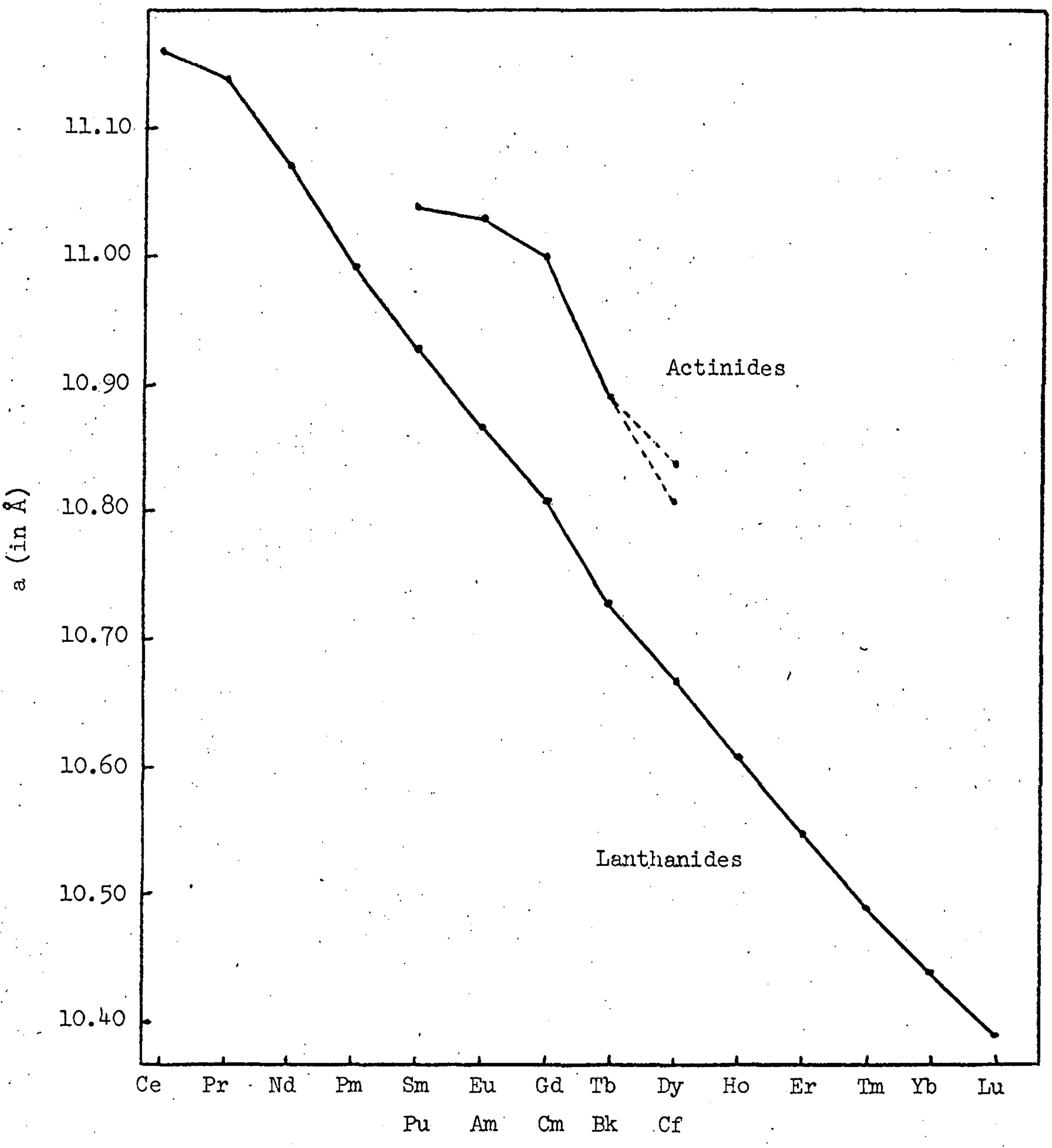

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Table VI. Crystal data for californium oxychloride.

Sample	Film	Observed		Observed	
		a(Å)[a]	2σ[b]	c(Å)[a]	2σ[b]
JC-II	2904A	3.956[c]	0.002	6.659[c]	0.005
JC-III	2736A	3.955	0.001	6.666	0.002
JC-IV	2782A	3.956	0.001	6.662	0.002

average[d] a = 3.956 ± 0.002Å c = 6.662 ± 0.009Å

[a] Calculated by LCR-2 computer program.

[b] Represents the 95% confidence range and reflects the internal consistency of the data for the particular sample.

[c] Based on data of one observer.

[d] Error limits on the average values were calculated using

$$95\% \text{ confidence error limits} = \frac{t}{\sqrt{N}}\sqrt{\frac{\Sigma(d_i)^2}{N-1}}$$

Table VII. Line list and indexing for tetragonal californium oxychloride - Film 2736A, JC-III

	2θ		Intensity	
hkl	calculated[a]	observed[b]	calculated[c]	observed[d]
101	26.20	26.21	10.00	10.0
002	26.75	26.76	1.32	5.0
110	32.00	31.96	5.79	10.0
111	34.78	34.81	0.53	5.5
102	35.21	35.16	6.48	10.0
003	40.60	40.56	0.81	4.5
112	42.18	42.16	2.45	7.0
200	45.88	45.86	2.68	8.5
103	46.90	46.86	0.37	1.5
201	47.98	48.01	0.52	4.5
113	52.60	52.61	2.13	7.0
211	53.60	53.66	3.13	9.0
202	53.91		0.84	
004	55.11	55.21	0.04	1.0
212	59.13	59.11	2.89	8.5
104	60.26	60.26	1.75	5.5
203	62.91	62.91	0.99	5.0
114	65.16	65.16	0.17	3.0
220	66.91	66.91	0.87	5.0
213	67.70	67.61	0.25	2.0
221	68.56	68.61	0.18	2.0
005	70.65	70.66	0.23	1.5
301	73.17	73.26	0.65	4.5
222	73.43		0.36	
204	74.45	74.46	0.06	1.0
105	75.21	75.26	0.21	1.5
310	76.10	76.06	1.03	4.5
311	77.67	77.86	0.15	4.0
302	77.92		0.67	

Table VII (continued)

	2θ		Intensity	
hkl	calculated[a]	observed[b]	calculated[c]	observed[d]
214	78.92	78.91	1.67	5.0
115	79.67	79.56	0.53	1.0
223	81.29	81.31	0.51	3.5[e]
312	82.34	82.36	0.72	3.5
303	85.67	85.66	0.07	1.0[e]
006	87.87	87.98	0.15	< 1.0
205	88.43	88.41	0.53	2.0
313α_1	89.93	89.91	0.69	5.0
321α_1	90.73	90.76	0.55	4.5
224α_1	91.95	91.96	0.03	< 1.0
106α_1	92.13		0.05	
215α_1	92.68	92.76	0.18	3.0
322α_1	95.33	95.36	0.62	5.0
304α_1	96.31	96.46	0.39	4.5
116α_1	96.49		0.30	
314α_1	100.70	100.91	0.09	2.0
400α_1	102.33	102.36	0.25	2.0
401α_1	103.90	103.96	0.05	< 1.0
206α_1	105.35	105.36	0.34	3.0
225α_1	105.92	106.01	0.30	3.0
411α_1	108.43	108.51	0.48	4.0
402α_1	108.69		0.14	
216α_1	109.91	110.51	0.10	1.0
305α_1	110.50		0.08	
330α_1	111.42	111.51	0.22	1.0
107α_1	112.60	112.66	0.40	1.0
412α_1	113.34	113.26	0.60	3.0
324α_1	114.41	114.42	0.77	2.5
315α_1	115.22	115.22	0.52	1.0

Table VII (continued)

hkl	2θ calculated[a]	2θ observed[b]	Intensity calculated[c]	Intensity observed[d]
$403\alpha_1$	116.99	116.97	0.26	1.5
$332\alpha_1$	118.17	118.27	0.19	1.0
$420\alpha_1$	121.13	121.07	0.54	3.5
$420\alpha_2$	121.63	121.67	0.27	1.5
$421\alpha_1$	122.93	122.87	0.12	2.0[e]
$421\alpha_2$	123.46	123.52	0.06	< 1.0[e]
$226\alpha_1$	124.62	124.67	0.39	2.0
$226\alpha_2$	125.16	125.27	0.19	1.0
$333\alpha_1$	127.27	127.22	0.36	2.0
$333\alpha_2$	127.85	127.82	0.18	< 1.0
$422\alpha_1$	128.59	128.57	0.34	1.0
$422\alpha_2$	129.19	129.28	0.17	< 1.0
$404\alpha_1$	129.85	129.88	0.03	< 1.0
$325\alpha_1$	130.81	130.72	0.21	1.5
$325\alpha_2$	131.44	131.52	0.11	< 1.0
$217\alpha_1$	133.45	133.47	1.06	3.5
$217\alpha_2$	134.11	134.42	0.53	2.0
$414\alpha_1$	135.78	135.87	1.06	5.0
$316\alpha_1$	136.04		0.81	
$414\alpha_2$	136.48	136.87	0.53	2.0
$316\alpha_2$	136.75		0.41	
$423\alpha_1$	139.23	139.22	0.76	3.5
$423\alpha_2$	140.00	140.02	0.38	1.5
$108\alpha_1$	141.71	141.42	0.11	< 1.0
$108\alpha_2$	142.53	142.52	0.06	< 1.0
$118\alpha_1$	149.40	149.47	0.55	1.0
$118\alpha_2$	150.45	150.52	0.28	< 1.0
$405\alpha_1$	151.78	151.72	0.66	1.5
$405\alpha_2$	152.93	153.07	0.33	< 1.0

Table VII (continued)

	2θ		Intensity	
hkl	calculated[a]	observed[b]	calculated[c]	observed[d]
501_{α_1}	157.35	157.22	0.67	5.5
431_{α_1}	157.35		1.35	
501_{α_2}	158.82	158.87	0.34	3.0
431_{α_2}	158.82		0.67	
424_{α_1}	160.77	160.62	0.18	1.0
326_{α_1}	161.32		0.34	
415_{α_1}	163.14	163.22	0.64	2.0

[a] Calculated using a = 3.955 Å, c = 6.666 Å, CuKα (λ = 1.54178 Å), CuKα_1 (λ = 1.54051 Å), and CuKα_2 (λ = 1.54433 Å).

[b] Averaged readings of two independent observers.

[c] Calculated using the POWD intensity program assuming the atomic coordinates of PbFCl. Calculation is scaled so that the strongest line has an intensity of 10.0.

[d] Averaged reading of two independent observers estimated visually on a scale from 10 to 1.

[e] Mixed with a platinum line.

Fig. 9. Lattice Parameters of Tetragonal Lanthanide and Actinide Oxychlorides.

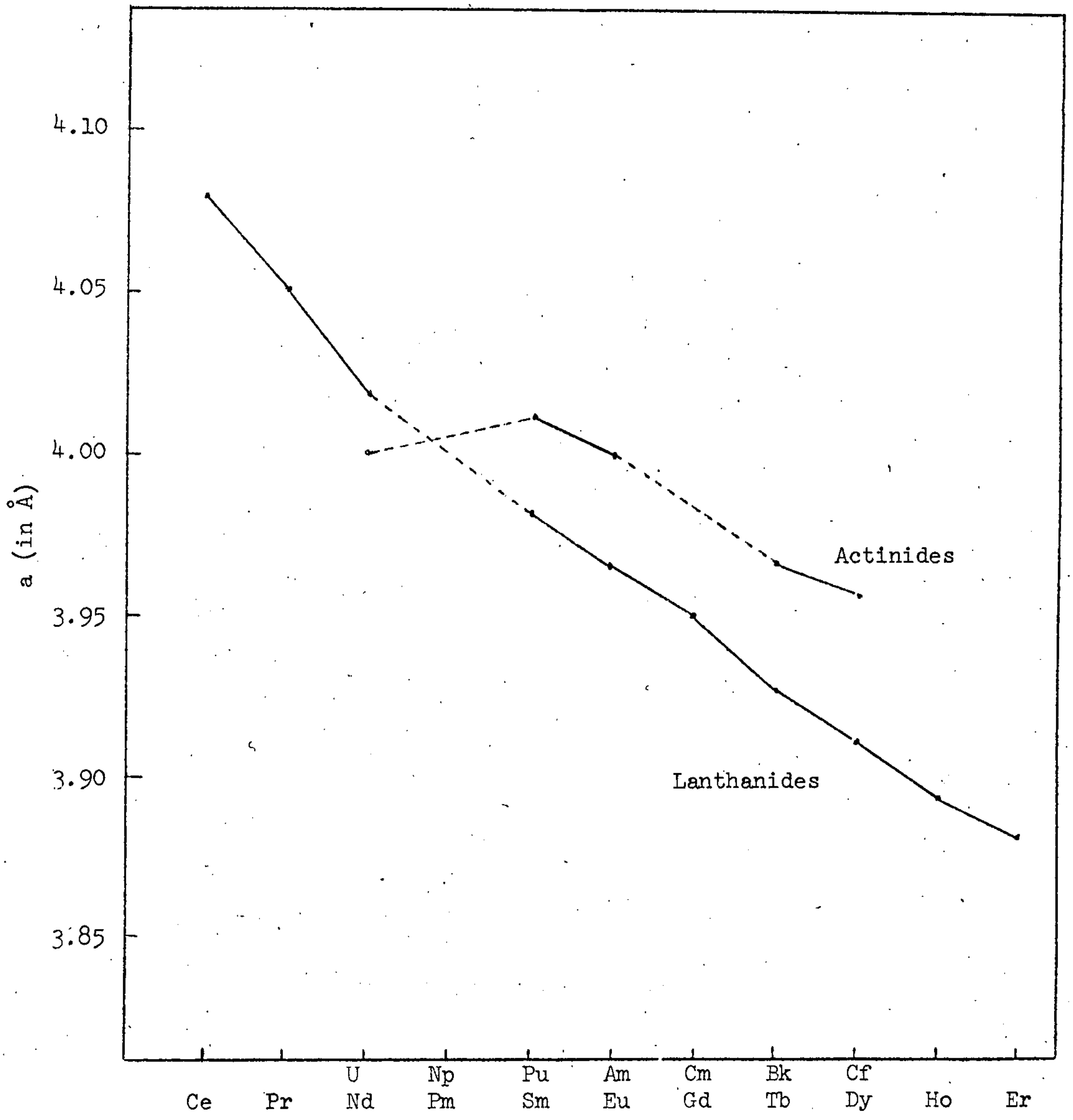

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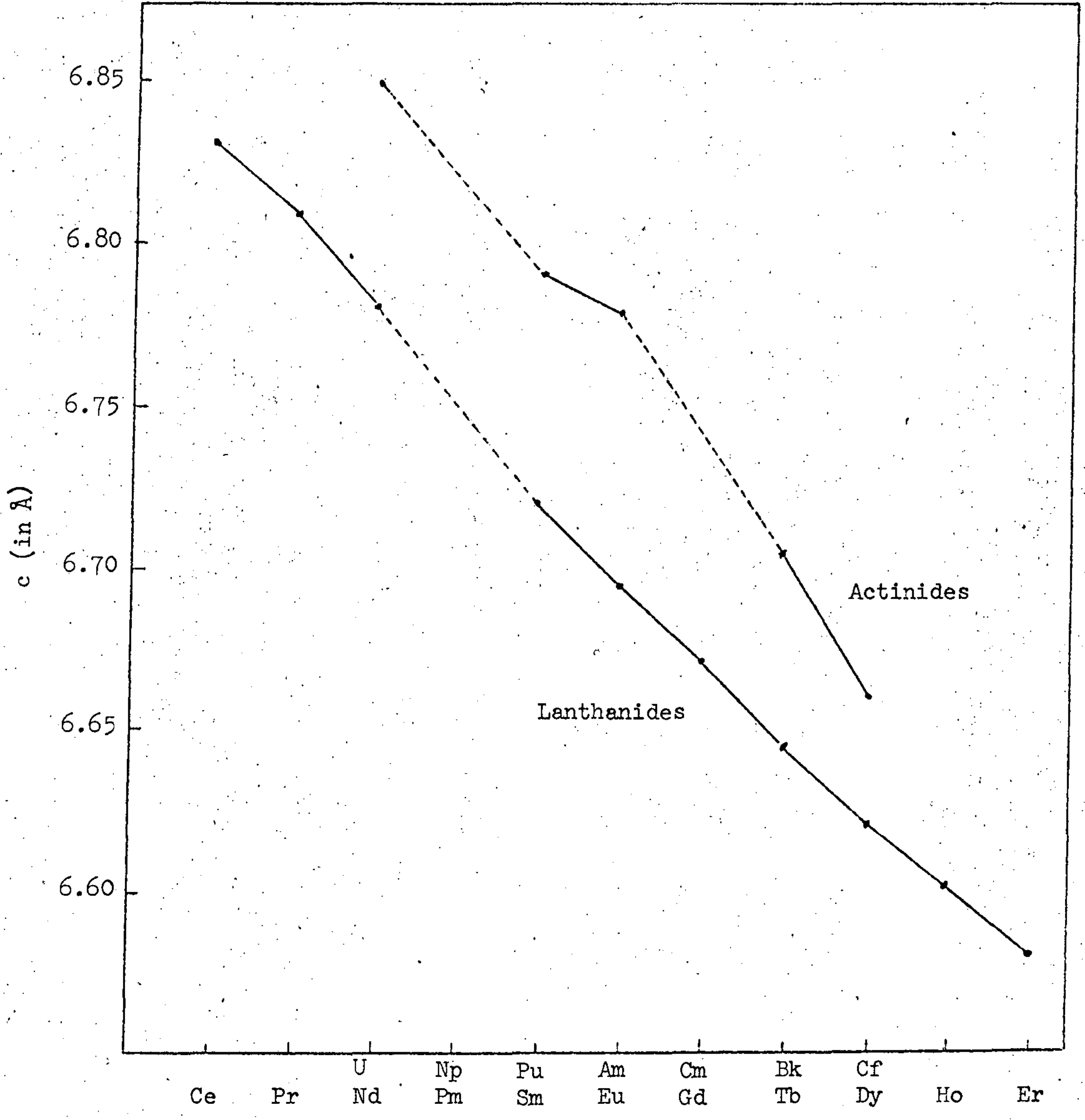
Fig. 10. Lattice Parameters of Tetragonal Lanthanide and Actinide Oxychlorides.



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single determination on a sample of BkOCl containing 5.16 atom percent californium and 0.27 atom percent cerium.[26] The reason for the unexpected shape of the curve in the early actinide region should be investigated more thoroughly.

VI. SUMMARY

The increasing availability of californium, element 98, has made study of some of its chemical and physical properties possible. In the present study, a low-temperature californium oxide of near-sesquioxide stoichiometry and californium oxychloride were prepared and studied by x-ray diffraction techniques. Originially 6 μg of Cf^{249} were purified by other workers using standard ion exchange techniques. A variety of analytical methods were used at that time to evaluate the purity of the sample. The results indicated 0.27 atom percent Nd and an estimated 1.60 atom percent total rare earths. Cu^{244} was estimated at < 1 atom percent, Am < 1 atom percent, and Pu was considered to be absent. Other materials, possibly Ca and/or Al, were considered to be potentially present. Radioactive decay of Cf^{249} from the time of the purification until this work produced 0.50 atom percent Cm^{245} as a contaminant.

Three samples of the low-temperature, cubic, Mn_2O_3-type californium "sesquioxide" were prepared and analyzed crystallographically. Two samples were produced by a hydrolysis reaction and had the same lattice parameters, within the error limits, the average of which was 10.838±0.02 Å. The third sample reacted in oxygen had the lattice parameter a = 10.809±0.003 Å. In an earlier study, the lattice parameter of an air-ignited sample was significantly smaller than the parameter after the same sample was heated in hydrogen. If these differences in lattice parameter reflect varying stoichiometries, then this might be evidence for higher and/or lower oxidation states of californium. The exact stoichiometries of the oxide samples prepared in this study are not known.

Three samples of californium oxychloride were prepared and analyzed by x-ray diffraction techniques. The CfOCl samples had the tetragonal PbFCl-type structure with averaged lattice parameters of a = 3.956±0.002 Å and c = 6.662±0.009 Å.

The error limits reported for the lattice parameters of CfOCl and the "Cf_2O_3" from the hydrolysis reactions are based on a statistical analysis of the consistency of the group of measurements. The error limits placed on the lattice parameter of "Cf_2O_3" sample from the reaction with oxygen represent the 95% confidence level and reflect the internal consistency of the data for that particular sample.

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