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SOME CHEMICAL PROPERTIES OF ELEMENT 97

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UCRL-17337

UNIVERSITY OF CALIFORNIA

Lawrence Radiation Laboratory
Berkeley, California

AEC Contract No. W-7405-eng-48

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Jospeh R. Peterson and Burris B. Cunningham

January 16, 1967

Meeting of the American Nuclear Society, San Diego, California, June 11-14, 1967.

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As part of a continuing program at this laboratory to investigate the chemical and physical properties of the heavy actinide elements and their compounds, a study of element 97 has been undertaken.

To date these investigations have included solution absorption studies of the tripositive berkelium ion and the preparation and crystallographic characterization of the berkelium oxides, trichloride, oxychloride, and fluorides.

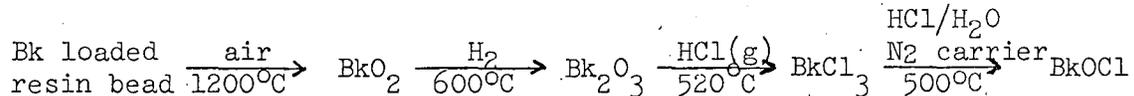
The most successful absorption experiments were carried out using a newly-developed microabsorption cell, consisting of two small (100 μ diameter) quartz rods between which was placed a small volume of Bk^{+3} (aq) solution (3-5 nanoliters containing 4 μg Bk^{249}). A suitably-modified Cary Model 14 Recording Spectrophotometer served as the measuring device, yielding spectra with 15 peaks between 320 and 700 $\text{m}\mu$. The two strongest peaks observed were at 417 and 474 $\text{m}\mu$. The observed spectral features are in excellent agreement with those seen by Gutmacher et al.¹ at the Livermore branch of the Lawrence Radiation Laboratory.

An attempt to observe the tetrapositive berkelium solution absorption spectrum by electrolytically oxidizing the Bk^{+3} (aq) solution while loaded on the cell was unsuccessful. It was concluded that the failure resulted from the bulk

solution acting as a reducing medium upon the tetrapositive berkelium ions formed locally at the anode.

About 16 μg of Bk^{249} were recovered and purified by extraction from an aqueous nitrate solution with di-(2-ethylhexyl)orthophosphoric acid, followed by stripping of the organic phase with a peroxide in nitric acid solution. The aqueous berkelium solution was then further purified by standard ion-exchange techniques. Mass analysis determined total cerium and neodymium content to be 0.27 and 0.06 atom per cent, respectively.

This purified material was absorbed on Dowex 50 (ca. 10 ppm ash) resin beads of about 200 nanogram capacity each. Employing the techniques described by Cunningham² and Green,³ the following series of reactions was performed to prepare the indicated berkelium compounds:



The fluorides were prepared from the oxides by reaction with H_2/HF mixtures and F_2 gas. Several independent samples (all containing ≥ 95 atom per cent Bk^{249}) of these compounds were characterized by use of x-ray powder techniques. BkO_2 exhibited the face-centered cubic (fluorite) structure; Bk_2O_3 , the Mn_2O_3 -type body-centered cubic structure; BkCl_3 , the UCl_3 -type hexagonal structure; BkOCl , the PbFCl -type tetragonal structure; and BkF_3 appeared to exhibit two stable modifications, the YF_3 -type orthorhombic structure and the LaF_3 -type trigonal structure, the latter one being the high temperature form.

Comparisons between the lattice parameters of these berkelium compounds and other similar actinide compounds consistently show evidence of the so-called "actinide contraction." Similar comparisons to corresponding lanthanide compounds and the behavior of the berkelium-fluorine system provide additional important evidence for the continuing rare-earth-like character of the actinide elements beyond the point of the half-filled 5f subshell.

REFERENCES

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