THE SPECTROCHEMICAL ANALYSIS OF HAFNIUM AND ZIRCONIUM

John G. Conway and Milton F. Moore

March 16, 1949

This document has been declassified by authority of issuing installation. Letter dated 6-18-49 Noted by MGH

Berkeley, California
The Spectrochemical Analysis of Hafnium and Zirconium

John G. Conway and Milton F. Moore
Radiation Laboratory, University of California
Berkeley, California

Abstract

The analysis of hafnium and zirconium by the copper spark technique is presented for solutions of HCl, HF and HClO₄ acids. The special techniques of electrode protection and vacuum drying of perchloric acid samples are outlined. Also given are the working curves and deviations of both elements.
The Spectrochemical Analysis of Hafnium and Zirconium

John G. Conway and Hilton F. Moore

Radiation Laboratory, University of California
Berkeley, California

Part I In Hydrofluoric and Hydrochloric Acids

Introduction

The difficulty in analyzing trace quantities of hafnium in zirconium and zirconium in hafnium has long been known. The specific nature of spectrochemical analysis offers one of the more promising solutions to the problem. In this paper a method is presented for analyzing hafnium and zirconium in hydrofluoric or hydrochloric acids solutions up to two molar.

Procedure

The essential method is that of the copper spark\(^{(1,2)}\). The electrodes are 1/4" diameter copper rod cut into 2" lengths, one end of which is machined flat across the diameter and along the sides for approximately 1/2" from the end.

A pair of electrodes are then transferred to an evaporator which consists of 4 to 5 turns of \#22 Nichrome wire. Ten such coils are connected in series and a current of two amperes is passed through them. The sample is then discharged onto the flat machined surface by means of a micro pipet and control and allowed to dry.

Four standard solutions were made containing .01 g/l of hafnium or zirconium ions in two molar HF and two molar HCl. The standards were treated in the same manner as the samples. After the series of samples and standards are thoroughly dried they are ready for sparking.

Standards are run in quadruplicate and samples in duplicate provided there is sufficient material. It has been found that up to 70 micrograms of either hafnium
or zirconium can be completely burned off in the 60 second sparking.

Equipment

A Baird Eagle Mount spectrograph is used with an Applied Research Laboratory spark source at a power setting of 2 KVA, 0.36 mh. inductance and 100 volts in the primary. Eastman Spectrum Analysis #1 photographic plates are used and developed for 3 minutes in D-19 at 20° C. A slit width of 50 microns, a 4 mm. analytical gap, and a sparking and exposure time of 60 seconds are used. The photographic film is calibrated using an iron arc and a step sector and densitometered using an Applied Research Laboratories Comparitor-Densitometer.

Results

Working curves are constructed in the usual manner and background correction made for each line. Two different internal standards, titanium and bismuth were tried, but it was found that neither helped to correct variations in the working curves. That is, when a curve of intensity ratio of the element to internal standard is plotted against concentration, the scattering of the experimental points is no better than when the intensity of the element is plotted directly against concentration. The most likely cause of this difficulty is that the spark source is not powerful enough to handle this particular problem.

Figure 1 shows the working curves obtained in which each point represents the average of six determinations. The average deviation from the mean for hafnium is 4.4% and for zirconium is 7%. To obtain such values the electrode alignment and sparking conditions must be rigidly controlled.

Upon repeating the standardization experiments six months later it is found that the curves are within 10% of each other. The break down of the internal standard method under these conditions is a very disturbing problem, however, the overall stability of the method and the incorporation of standards on each plate makes it possible to perform an analysis.
To do an analysis when the ratio of one element to the other is between 100/1 and 800/1, samples of two different sizes must be taken. The sample size is chosen so as to fall as near to the middle of the working curve as is possible.

Part II In 2 Molar Perchloric Acid

Introduction

The spectrographic analysis of hafnium and silicomium in perchloric acid presents many difficult problems not usually encountered in the analysis of solutions. The main difficulty encountered is the chemical reaction between the electrodes and $\text{HClO}_4$. Platinum or gold electrodes in sufficient quantities necessary for such work is prohibitive in cost. Acid resistant paint and evaporation in vacuum offers a solution to this problem.

Procedure

The copper electrodes used have the advantage that they are not expensive and available in sufficient quantities for this work.

Electroplating a thin film of gold on the end of the machined copper electrode was tried, but even the best plated electrodes had small pin holes through which the acid would attack the copper. This etching became greater upon concentration of the acid by evaporation in the drying process. The salts formed by this etching are in such quantities that mechanical dislodgment occurred when the spark first struck. The salts also increased the background to such an extent that it was impossible to densitometer the lines.

Since platinum was not available in sufficient quantities and the above method did not work, it was decided to try acid resistant paints. Several were found satisfactory, the best of which is a vehicle from a paint known as Prufoost. For use in this work the Prufoost has to be diluted with six parts of benzene.
A freshly machined copper electrode is dipped into the diluted Prufcoat to a depth of one half-inch, withdrawn and placed upright in a holder to dry. This drying may be accelerated by heating. The dried electrodes are then placed in a copper block and the samples and standards are discharged onto the protective coat. If the volume of the sample or standard is too large to be placed on the electrode at one time it may be reduced by placing the electrodes in the evaporator and heating. The solution should not be permitted to go to dryness in air because the action of the perchloric acid is enough to decompose the protective coat. The partially dried samples and standards are transferred to a copper electrode holder and this placed in a vacuum dessicator which is then evacuated to between 0.2 and 0.5 mm of Hg and held there until the solution dries. This drying in vacuum may be hastened by irradiation the copper block and electrodes with an infra-red lamp. The reason for the vacuum drying is that perchloric acid does not distill undecomposed in air, but does at reduced pressures (4). Calcium chloride is used as a drying agent in the dessicator.

The dried electrodes are kept in the dessicator until ready to use because of the hygroscopic nature of the sample. The electrodes, once they are dry, are sparked in the same manner as was described in Part I. Since the protective coat increases the background to some extent, the more sensitive line 3392A of zirconium is used and photographed in the second order with a slit width of 25 microns.

Results

The working curves are plotted in the usual manner and in all cases it is necessary to make background corrections. Figures 2 and 3 show the working curves for hafnium and zirconium using perchloric acid. Because of the added material the variation in reproducibility is greater. The deviation from the mean for hafnium is 11% and that for zirconium is 15%. A weak copper line is
FIGURE 3

HF IN HClO₄ ON PRUFCOAT

HAFNIUM 3072 A

INTENSITY

CONCENTRATION (MICROGRAMS)
Found to interfere with the 3392 zirconium line at low concentrations and must be corrected for in the working curves.

References

3. Prufcoat Laboratories Inc., 50 East 42nd St., New York, N. Y.