[CONTRIBUTION NO. 102 FROM THE INSTITUTE FOR ATOMIC RESEARCH AND DEPARTMENT OF CHEMISTRY, IOWA STATE COLLEGE]

The Adsorption Separation of Zirconium and Hafnium[1]

BY ROBERT S. HANSEN, KEITH GUNNAR, ALFRED JACOBS AND C. ROBERT SIMMONS

Since the discovery of the element hafnium by Coster and Hevesy in 1923,[2] the attendant realization of its chemical similarity to zirconium and its invariable coöccurrence with the latter element, numerous methods have been devised for their separation. Of the fractional precipitation methods, the phosphate,[2,3] potassium and ammonium double fluoride,[2] and ferrocyanide,[4a,b] methods appear to have been most successful. Recently, two liquid–liquid extraction separation methods have been published, one involving the distribution of the thiocyanate complexes between ether and aqueous phases,[5,6] the other the distribution of the thenoyltrifluoroacetone complexes between benzene and aqueous phases.[7] Street and Seaborg have recently published an ion exchange separation.[8]

None of the fractional crystallization methods could be said to constitute simple procedures for preparation of appreciable quantities of hafnium-free zirconium. All require repeated operations, and the phosphates in addition are not readily converted to other compounds which might be of interest. The liquid–liquid extraction methods can be adapted in principle to continuous flow operation, but such adaptation is at least not simple at the laboratory scale where a large number of plates is required. The ion exchange separation has been claimed suitable for use with gram quantities but has not been tested for larger quantities. The method requires a comparatively high acidity due to the tendency of zirconium and hafnium to form colloids at lower acidities.

The amount of hafnium occurring with zirconium is not large; the hafnium to zirconium weight ratio varies from 0.007 to 0.05 in common ores and is about 0.023 in the most common American ore. Under these circumstances a purification method based on an adsorption process specific or at least strongly preferential for hafnium should be an extremely useful and simple method for purification of zirconium from hafnium, and for the concentration or possibly the preparation of hafnium.

Such a method was recently discovered in our laboratory.[9] It was found that silica gel adsorbs hafnium with strong preference from a methanol solution of the tetrachlorides,[10] and that this fact furnishes a basis for adsorption column purification of zirconium from hafnium. The object of the present paper is to discuss this process more completely, including recent extensions.

Our most satisfactory results were obtained by the following procedure:

A column is prepared using a good grade silica gel 28–200 mesh activated two hours at 300°. This is conveniently done by sludging the gel in methanol and pouring the sludge into the column.

Zirconium and hafnium tetrachlorides are dissolved in methanol in the proportion 1 g. of tetrachloride per 5 ml. of methanol. This solution is then fed through the column, preferably from bottom to top, and the effluent collected. By suitable choice of conditions the effluent zirconium can be obtained with the hafnium content as low as desired. The zirconium can be recovered by distillation of the methanol, solution of the residue in water, and separated from common impurities, notably iron, titanium and aluminum by crystallization of the oxychloride.[11]

Figure 1 indicates typical results obtained. It will be observed that appreciably better results are obtained on a larger scale operation; since curves 1 and 2 correspond to very nearly the same linear velocity of solution through the column, the difference does not appear to be a flow rate effect. Results in good agreement with curve 2 have been obtained with 4″ diameter columns containing 12 lb. silica gel and with columns 6″ in diameter containing 40 lb. gel. It therefore appears that curve 2 represents the performance to be expected in an intermediate or large scale operation.

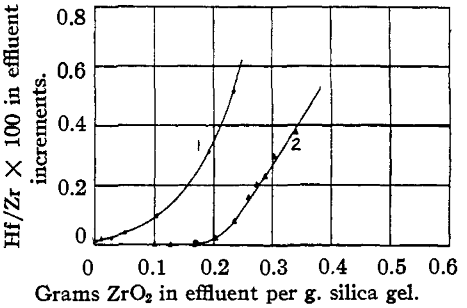

Fig. 1.—Comparison of column size in Zr–Hf separation: curve 1, 50 mm. diam. × 4 ft. length—1 kg. silica gel; curve 2, 4 in. diam. × 5 ft. length—8 kg. silica gel.

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[1] Presented at the 117th National Meeting of the American Chemical Society, Houston, Texas, March 28, 1950.

[2] Coster and Hevesy, *Nature*, **111**, 79, 182, 252, 462 (1923).

[3] Willard and Freund, *Ind. Eng. Chem.*, *Anal. Ed.*, **18**, 195 (1946).

[4] (a) Prandtl, U. S. Patent 1,976,293 (1934); (b) Schumb and Pittman, *Ind. Eng. Chem.*, *Anal. Ed.*, **14**, 512 (1942).

[5] Fischer and Chalybaeus, *Z. anorg. Chem.*, **255**, 79 (1947).

[6] Fischer, Chalybaeus and Zumbusch, *ibid.*, **255**, 277 (1947).

[7] Huffman and Beaufait, THIS JOURNAL, **71**, 3179 (1949).

[8] Street and Seaborg, *ibid.*, **70**, 4268 (1948).

[9] Hansen and Gunnar, *ibid.*, **71**, 4158 (1949).

[10] As a result of reactions between metal tetrachlorides and methanol the solution contains, in addition to the metal tetrachlorides, substantial quantities of methoxy metal trichlorides and hydrogen chloride.

[11] Young and Vander Weyden, "Inorganic Syntheses," Vol. II, McGraw-Hill Book Co., Inc., New York, N. Y., 1946, p. 119.

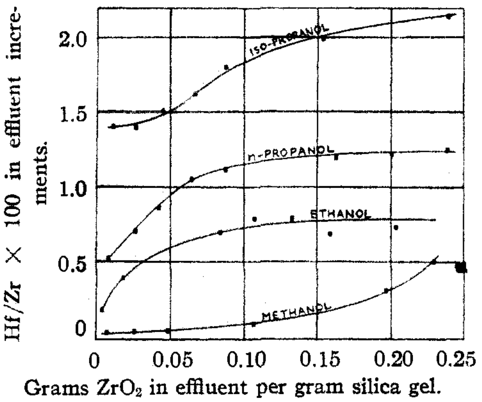

Fig. 2.—Effect of solvents upon Zr–Hf separation; feed conditions: 600 g. $ZrCl_4$ in 3000 ml. solvent—2.35% Hf/Zr; columns, 50 mm. × 4 ft. length—1000 g. silica gel.

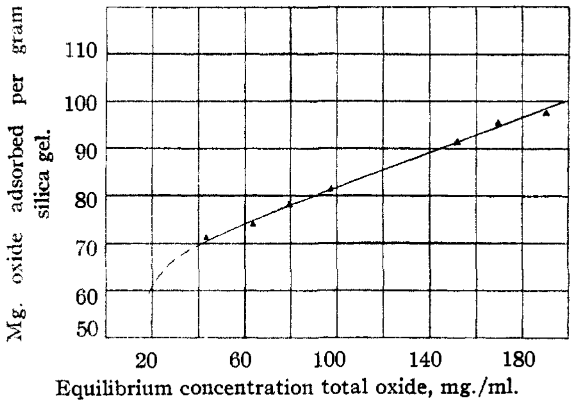

Fig. 3.—Adsorption isotherm for batch adsorption at 20°: 50 ml. $ZrCl_4$–CH_3OH solution, 25 g. silica gel.

It should perhaps be emphasized that it is a waste of time and material to feed into the column more solution than the gel will purify. If the feed material has a hafnium/zirconium ratio of 0.02 and a product spectroscopically free from hafnium is desired, this amount is not greater than 1 lb. of zirconium dioxide per 5 lb. of silicon dioxide. After this quantity of zirconium dioxide has entered the column, pure methanol can be used to flush it through. The following appear to be important factors in the successful operation of the procedure.

(1) **Silica Gel.**—Good grade commercial silica gels are satisfactory. Activation is an important step; the yield of low hafnium product is approximately halved if the gel is not activated. Gel properties affected by this activation have been discussed extensively by Bartell and Almy,[12] and the procedure used was that recommended by them. Three different silica gels were used, all of approximately 720 square meters per gram surface area. Two had total non-volatile impurities of approximately 0.3% and gave very similar results; a third contained approximately 1% non-volatile impurities and gave much poorer results.

(2) **Solvent.**—Methanol, acetone, acetic acid, water, ethanol, *n*-propanol, isopropyl alcohol and ethyl acetate were investigated. Slight preferential adsorption of hafnium from acetic acid solution of zirconium and hafnium tetrachlorides was observed, none from water solution. Preferential adsorption of hafnium from acetone solution was found to be strong, but the tetrachlorides degraded the acetone, and the tarry products formed tended to clog the columns. Of the alcohols, methanol gave by far the best results; the comparison is given in Fig. 2.

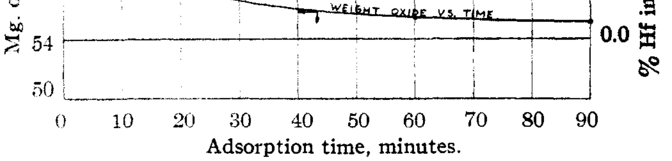

Fig. 4.—Kinetics of batch adsorption of $ZrCl_4$ solution: 41 g. $ZrCl_4$ in 322 ml. methanol–100 g. silica gel.

Procedure Followed in Obtaining Kinetics Data.—A solution of 41 g. of $ZrCl_4$–$HfCl_4$ in 322 ml. of methanol was added to 100 g. of activated silica gel in a flask. The flask was placed in an automatic shaker and aliquots were removed at various time intervals; these aliquots were weighed as the oxides and analyzed spectroscopically for per cent. hafnium.

(3) **Concentration.**—Zirconium tetrachloride is soluble in methanol at least to the extent of 1 g. per ml.; at concentrations this high the solution is extremely viscous. It is probable that at least some of the alkoxy substituted compounds are formed; based on conductivity measurements assuming the conductivity of the methanol solution due solely to the hydrogen chloride the equilibrium constant for the first substitution was estimated at 0.1. On this basis it would appear that in a 1 *M* solution of the tetrachloride in methanol approximately 30% of the zirconium is present as methoxy zirconium trichloride. The complexity of the solution makes the interpretation of adsorption data difficult. Representative data are given in Fig. 3. In column operation, 20% solutions of the tetrachloride were found to give optimum results. Concentrations of from 15–25% gave quite similar results: concentrations of 40% gave very poor results, and concen-

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[12] Bartell and Almy, *J. Phys. Colloid Chem.*, **36**, 475 (1932).

trations of 10% gave results significantly poorer than the optimum.

(4) **Flow Rate.**—Figure 4 shows that the adsorption process is by no means instantaneous, and that therefore a slow flow rate is desirable for optimum column utilization. For columns packed with 28–200 mesh silica gel it was found that flow rates of 20 cm./hour based on the empty column were satisfactory; slower flow rates did not produce appreciable improvement in results.

It remains to investigate the possibility of concentration of hafnium by differential stripping of the silica gel. If a column is operated until the last effluent increment has a weight Hf/Zr ratio of 0.003, the last product being flushed out with methanol and the column drained, the silica gel will contain approximately 0.1 g. total oxide equivalent per gram silica gel, of which approximately 10% is hafnium oxide. Prolonged flushing with methanol (until effluent gives no further qualitative test) removes approximately one-half of the zirconium but very little hafnium, so that there remains on the gel 0.05 g. total oxide equivalent per gram silica gel, of which 20% is hafnium oxide. Further concentration can be obtained by stripping with 2.5 *M* anhydrous HCl in methanol; it is advantageous to use this solvent from the start of the stripping operation since less time and material are required to achieve the concentration from 10 to 20% than with pure methanol. The differential stripping is illustrated by Fig. 5. Nearly 90% of the adsorbed hafnium can be recovered as a 20% hafnium oxide–80% zirconium oxide product, 60% as a 30% hafnium oxide product, or about 20% as a 60% hafnium oxide product. It is not believed that further differential stripping is worthwhile because of rapidly decreasing yields. A concentrate in the 30–60% hafnium oxide range should be a highly satisfactory starting material for a liquid–liquid extraction concentration, however.

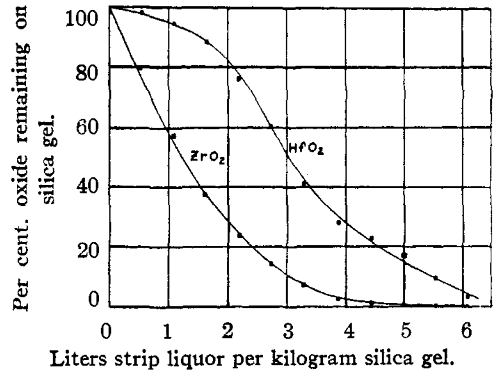

Fig. 5.—Differential stripping of Zr and Hf from silica gel with 2.5 molar HCl in methanol—120 lb. gel.

Final stripping is best achieved by use of an aqueous 7 *N* H_2SO_4 solution. Such stripping requires less than half the volume required for 2.5 *M* HCl in methanol, but is not differential. The silica gel can be reactivated and used again.

Acknowledgment.—Spectrographic analyses were performed by the spectrographic laboratory of the Ames Laboratory, A. E. C. under the supervision of and according to a method developed by V. A. Fassel and C. H. Anderson. The assistance of these workers is gratefully acknowledged. This work was performed in the Ames Laboratory, Atomic Energy Commission.

Summary

An adsorption purification of zirconium from hafnium has been discovered. Most satisfactory results have been obtained from the preferential adsorption of hafnium from a methanol solution of zirconium and hafnium tetrachlorides by silica gel. Other solvents have been investigated, as well as effects of concentration, flow rate and gel properties. Concentration of adsorbed hafnium to 30–60% products in good yields has been achieved by differential stripping.

AMES, IOWA RECEIVED MAY 11, 1950

[CONTRIBUTION FROM BALLISTIC RESEARCH LABORATORIES, ABERDEEN PROVING GROUND, MD.]

Chemiluminescence of the Sodium or Sodium Halide Catalyzed Oxidation of Carbon Monoxide by Nitrous Oxide[1]

BY CHARLES P. FENIMORE AND JOHN R. KELSO

While Bawn[2] showed that the oxidation of carbon monoxide by nitrous oxide involves both heterogeneous processes and gas phase chain reactions, he did not study the effect of varying the nature of the surface. There are marked differences between the reactions in sodium halide coated and in clean vessels; although the most interesting differences appear to be due not to a variation in the heterogenous reaction, but to a small amount of sodium vapor in the gas phase (formed from the sodium halide), and to the reluctance of nitrous oxide to transfer its oxygen atom directly to carbon monoxide. We suggest that free sodium atoms catalyze the oxidation of carbon monoxide with simultaneous emission of the sodium resonance lines. We formulate the catalysis

$$Na + N_2O \longrightarrow NaO + N_2$$
$$NaO + CO \longrightarrow CO_2 + Na^*(^2P)$$
$$Na^* \longrightarrow Na + h\nu$$

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[1] Presented at the American Chemical Society meeting in Detroit, Mich., April, 1950.

[2] Bawn, *Trans. Far. Soc.*, **31**, 461 (1936).