ration of high-purity oxides by means of a recrystallization process employing sulfuric acid had been proposed by Clabaugh and Gilchrist.[6] This is perhaps the best method published for obtaining very high-purity zirconium compounds. It involves the formation of zirconium sulfate tetrahydrate ($Zr(SO_4)_2 \cdot 4H_2O$) by the addition of concentrated sulfuric acid to a fairly concentrated aqueous solution of zirconium sulfate or zirconium chloride. Small amounts of hydrochloric acid are required in the sulfate solution to insure the removal of iron. A 70% recovery of zirconium is claimed after five recrystallization steps.

Preparation of the Oxychloride

During the course of preparing large amounts of high-purity zirconium oxide for the analytical laboratory, it became evident that, by modifying the basic method of Herzfield, it was possible to recover at least 90% of the valuable metals (even after losses occasioned by several recrystallization steps). A curdy precipitate forms upon the addition of a saturated aqueous solution of zirconyl chloride to an acetone–hydrochloric acid mixture. Readily filterable, these crystals have been identified by X-ray diffraction to be zirconyl chloride octahydrate ($ZrOCl_2 \cdot 8H_2O$). To effect further recrystallization, the product can be dissolved readily in half its weight of water, then added to the acetone–hydrochloric acid mixture. The purified crystals form immediately and may be collected on a buchner funnel and washed with acetone. The recrystallization procedure may be repeated until the desired purity is obtained. The final oxychloride is ignited to the oxide by heating to 1000° for one hour. The spectrographic analysis of the zirconium samples produced indicated the presence of 20 p.p.m. each of aluminum, iron, copper, and silicon and less than 0.5 p.p.m. boron. No other elements except hafnium were detected. The average starting material contained the following impurities: 0.3% iron, 0.1% silicon, 100–1000 p.p.m. titanium and aluminum, and less than 100 p.p.m. copper. Comparable samples of high-purity hafnium have been analyzed with similar results. No heat is required in any phase of the process. The solutions are comparatively safe to handle and do not present a filtration or recovery problem.

The effect of the presence of acetone in the system is to decrease the solubility of the oxychloride in hydrochloric acid, thereby increasing the yield. However, enough acid must be added to provide a minimum normality of 4.5 to assure the high recovery.

The normality is based upon the acid entering the system in the acetone–acid mixture and the total volume of water in the zirconyl chloride solution. Figure 1 shows the effect of acidity upon the percentage of metal recovered for two ratios of acetone to zirconyl chloride. A third line is plotted to show the recovery expected without the use of acetone in the addition agent. The data for this curve were taken from the solubility curve of zirconyl chloride as found by Spink and Wilhelm.[5] The graph indicates that a higher percentage recovery of zirconyl chloride results as the ratio of acetone to metal increases. The presence of the acetone in this system greatly increases the filterability of the zirconyl chloride formed.

The optimum proportions for satisfactory recrystallization appear to be 1 ml. of saturated zirconyl chloride solution of 5 ml. of acetone and 1 ml. of concentrated hydrochloric acid. The crystals are collected in a buchner funnel, using a No. 7 Whatman filter paper. The cake is then washed a number of times with acetone and air-dried in the funnel. Using the procedure described above, 200 g. of zirconium tetrachloride, or 276 g. of zirconium oxychloride, was dissolved in water and recrystallized five times, producing 246.5 g. of high-purity material. The stepwise efficiency was 96–99% for an over-all recovery of 89.0%. Additional experimentation performed upon hafnium starting solutions have indicated that the same high purification will result for this metal also.

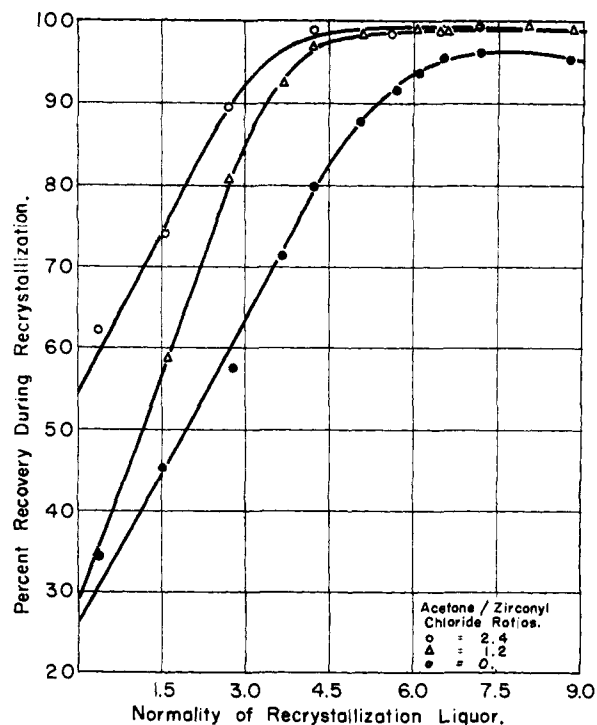The equipment employed in analyzing this material was a Baird 3-meter spectrograph. Each sample was burned

(6) W. S. Clabaugh and R. Gilchrist, THIS JOURNAL, 74, 2104 (1952).

Fig. 1.—Recrystallization yield for the system zirconyl chloride–acetone–HCl.

individually with high-purity graphite electrodes. The ignition area was thoroughly cleaned after each sample was burned. A sample of the product obtained by the sulfuric acid method of Clabaugh and Gilchrist was analyzed along with the oxides formed in this method. Each of the two products was as pure as was obtainable within the limits of detection of the method employed.

This simple purification method is believed to be suitable for laboratory preparation of either pure zirconium oxide or hafnium oxide. Metal recoveries of 96 to 99% per crystallization step are obtainable. This system can be employed in making superpure compounds from the oxides. The high metal recovery, as compared to that obtainable by the present methods, increases the possibility of expanding the process to pilot-plant or production-plant size. Recovery of the only expensive chemical, acetone, is feasible. The rapid manipulation of the process steps, the ease of filtration of the crystals, the absence of heating and cooling periods for crystallization, and the relative safety in handling chemicals are some of the many advantages of this system. The purity developed equals or exceeds that detectable by the usual spectrographic methods employed for analyzing zirconium oxides.

BUREAU OF MINES
ALBANY, OREGON

Titration of Polyacrylic Acid with Quaternary Ammonium Bases

BY HARRY P. GREGOR, LIONEL B. LUTTINGER AND ERNST M. LOEBL

In general, the titration behavior of acids (bases) is expected to be independent of the nature of the base (acid) with which it is titrated; this certainly holds for simple mono- and polybasic acids (bases). However, in the case of highly polyfunctional substances specific effects seem to play a role. Thus Steinhardt[1] and Tanford[2] observed that the titra-

(1) J. Steinhardt, Ann. N. Y. Acad. Sci., 41, 287 (1941).
(2) C. Tanford, THIS JOURNAL, 72, 441 (1950).

tion behavior of proteins depended on the specific acid or base used. Katchalsky[3] noted a difference in the viscosity behavior of polyacrylic acid neutralized with NaOH and KOH, respectively. It is reasonable to assume that these differences are caused by the extremely close associations of the gegenions with the polymer chain, due to the very high potential on the chain. A consequence of this

might be that the effect would depend strongly on the size of the gegenion.

In order to investigate this, polyacrylic acid was titrated with potassium hydroxide, tetramethylammonium hydroxide, tetraethylammonium hydroxide and tetrabutylammonium hydroxide in the absence and presence of neutral salts of the same bases.

A solution of pure polyacrylic acid (molecular weight range 30,000–100,000) was prepared in 0.0128 N concentration. Titrations were performed at 25° in CO_2-free atmosphere using a high pH glass electrode with standard solutions of the bases in the presence and absence of the corresponding (chloride or bromide) salts (0.01 N).

Figure 1a gives the titration curves in the presence of neutral salts; Fig. 1b shows the plots of pH vs. log $(1 - \alpha)/\alpha$ for the same cases. The curves in the absence of neutral salt are similar. It is seen that at low values of α the titration curves are similar, but diverge at higher values of α. Table I shows the pH values at half neutralization (pK_a) and the slopes of the best straight lines through the points in the logarithmic plot (n).

An inspection of the titration curves and the pK_a and n values in Table I shows that increasing the size of the cation of the base has the effect of weakening the apparent acid strength of the carboxyl groups; this effect increases with increasing degree of neutralization, as shown by an increasing divergence of the titration curves. The effect is due to the greater loss in electrostatic binding energy when the small hydrogen ion is replaced as a gegenion by a large rather than a small cation, and the fact that a small ion is more effective in shielding the chain than a large ion. Further experimental results involving this and other techniques and a quantitative treatment will be presented later. Parallel experiments on cross-linked polyacrylic acid[4] show similar effects.
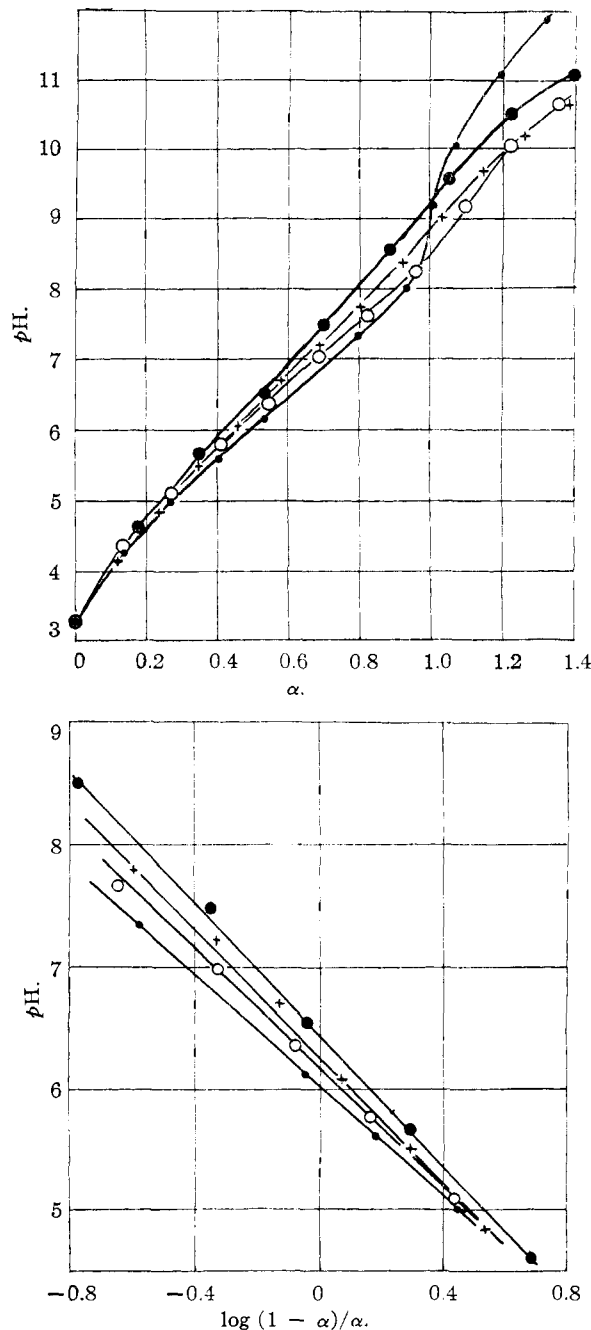

Fig. 1a and 1b.—Titration of 0.0128 N polyacrylic acid with: potassium hydroxide (●); tetramethylammonium hydroxide (O); tetraethylammonium hydroxide (+): tetrabutylammonium hydroxide (●). Titrations carried out in the presence of 0.01 M solutions of corresponding (halide) salt.

TABLE I

	Neutral salt absent pK_a	n	Neutral salt present pK_a	n
K^+	6.43	2.16	6.00	2.30
Me_4N^+	6.48	2.27	6.18	2.53
Et_4N^+	6.64	2.56	6.29	2.64
Bu_4N^+	6.85	2.69	6.54	2.75

(4) F. Bernstein, Dissertation, Polytechnic Institute of Brooklyn, 1952.

DEPARTMENT OF CHEMISTRY
POLYTECHNIC INSTITUTE OF BROOKLYN
BROOKLYN, NEW YORK

The Infrared Spectra of Tripropylsilane, Triphenylsilane and Triphenyldeuterosilane

BY LOUIS KAPLAN

Although the vibrational spectra of the trihalogenosilanes have been analyzed[1] in detail, there have been relatively few reports in the literature

(3) A. Katchalsky, J. Polymer Sci., 7, 393 (1951).

(1) See F. Halverson, Rev. Mod. Phys., 19, 87 (1947).