A CONDUCTOMETRIC INVESTIGATION OF THE
TITRATION OF AQUEOUS ZIRCONIUM
SOLUTIONS WITH FLUORIDE

by

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INTRODUCTION

Zirconium is usually determined by gravimetric procedures, all of which are quite slow and subject to a number of errors. Zirconium hydroxide may be precipitated from solution with ammonium hydroxide, ignited to the oxide, ZrO_2, and weighed (17, p.122). Diammonium phosphate precipitates zirconium from sulfuric acid solutions. The composition of the precipitate is too indefinite to permit ignition and weighing except for very small amounts of zirconium. The phosphate method is often employed for small amounts of zirconium. The composition of the ignited precipitate is approximately ZrP_2O_7 (17, p.123). An empirical factor, 0.3828, for converting the weight of ignited precipitate to zirconium has been proposed (17, p.123). Other precipitants used for zirconium include selenious acid (15, pp.921-933), cupferron, benzene arsonic acid, 8-hydroxyquinoline, p-hydroxyphenylarsonic acid, propyl arsonic acid, and mandelic acid (12, p.376).

Two volumetric methods for zirconium have been reported. Claassen (3, pp.252-261) precipitated zirconium with an excess of selenious acid. The basic selenite, $ZrOSeO_3$ is precipitated. Upon long digestion

in the presence of excess selenious acid, this precipitate
is converted to the normal selenite, $Zr(SeO_3)_2$. The
determination can be completed in either of two ways.
The normal selenite may be dried at 120-200° C and weighed
or the precipitate may be dissolved in a mixture of 6 ml
of 18N sulfuric acid and 5-10 ml of 3% sodium fluoride
solution. In this solution HI reduces the selenite to
elementary selenium according to the equation

$$SeO_3^= + 6 H^+ + 4 I^- \longrightarrow Se + 2 I_2 + 3H_2O$$
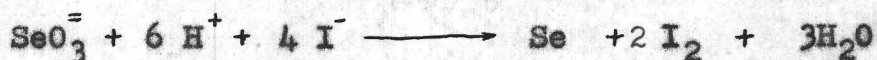
The iodine is then titrated with thiosulfate.

The second volumetric method is based on the
determination of the acid formed in the reaction of the
zirconium salt with sodium tartrate (19, p.1263). An
excess of sodium tartrate is added and the solution is
titrated in the cold with sodium hydroxide. Thymol-
phthalein indicator is used. The free acid is determined
in a separate portion of the solution. This is done by
adding a neutral solution of potassium fluoride saturated
with potassium chloride and potassium nitrate to the
sample and titrating with sodium hydroxide to a phenol red
end point. The zirconium content is calculated from the
amount of sodium hydroxide used to neutralize the acid
equivalent to the zirconium. This is obtained from the
difference in the amount of sodium hydroxide used in the
two titrations.

This work was undertaken in an attempt to develop a rapid volumetric method for the determination of zirconium. Since a major problem in working with zirconium is the ease of hydrolysis of its compounds, it was decided to use a conductometric method to determine the end point. The accuracy of conductometric methods is not affected by a marked hydrolysis, solubility, or dissociation of the reaction product (11, p.225). Conductometric methods may be used to determine the end point for reactions involving precipitations or complex formation. Since the fluoride complexes of zirconium are very stable (4, p.1), it was decided to study the titration of zirconium with sodium fluoride solutions.

THEORETICAL CONSIDERATIONS

The theory and application of conductometric analysis is discussed thoroughly in the monograph by Britton (2, pp.1-170) and in several review articles (11, pp.225-230), (16, pp.1793-1803), (10, pp.252-266). The chief applications of conductometric analysis are in the fields of titrations of weak acids and bases, or any acids and bases in colored solutions, or in the field of precipitation reactions. To a less extent it is used to follow complex formation and oxidation reduction reactions (7, pp.56-57).

If an electrolyte is added to a solution of another electrolyte without changing the volume appreciably, the conductivity increases provided the electrolytes do not react. If an ion from one electrolyte reacts with an ion from the other electrolyte to form a slightly dissociated or slightly soluble molecule, or changes the number of ions in solution by an oxidation-reduction process, the conductivity of the solution will change.

The conductivity will (1) decrease, (2) remain the same, or (3) increase depending upon the reagents and the reaction product. If the reaction product is slightly soluble the reaction may be expressed thus:

$$B^+ + A^- + C^+ + D^- \longrightarrow BD + A^- + C^+$$
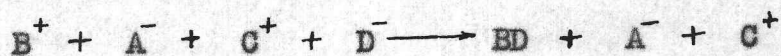
The ion to be determined is B^+. The reagent is $C^+ + D^-$. In the titration the B ions are replaced by C ions.

(1) If the mobility of the B ions is greater than the mobility of the C ions, the conductivity decreases until the equivalence point is reached, after which it increases.

(2) If the mobilities of B and C are equal, the conductivity remains the same until the equivalence is reached.

(3) The conductivity increases if a slightly dissociated substance is titrated and the reaction product is a strong electrolyte. Such is the case in the titration of a weak acid with a strong base. The conductance increases further after the equivalence point has been reached (11, p.225), (2, pp.43-68).

DETERMINATION OF END POINT. In a conductometric titration the conductance is measured after each addition of reagent. The points obtained are plotted on a graph and usually fall on two straight lines. The intersection of these lines gives the equivalence point. Data obtained near the equivalence point have no special significance and very often are worthless due to hydrolysis, dissociation, or solubility of the reaction product (11, p.225). In some cases it is more convenient to plot resistance against volume of titrant in place of

conductance.

A method for calculating the end point has been recommended by Corwin and Moyer as a means to avoid the inconvenience of plotting a graph to find the end point (6, p.303). In those cases where the angle between the two lines is not very sharp, graphical determination of the end point is not accurate. The equation for a straight line, $y = ax + b$, is used with x representing the number of milliliters of titrant and y representing the calculated resistance (or conductance) of the cell. Corwin and Moyer determined the slope, a, by picking two sets of readings before the equivalence point which are far enough from the region of curvature to assure a linear relationship. The value of a was then used to calculate the constant, b, for each reading. An average of these b values was then used with the value of a to give the equation of the line before the equivalence point. In a similar manner the equation for the line after the end point was calculated. The simultaneous solution of these two equations for x gives the volume of titrant at the equivalence point. In this work it was found better to calculate the a values for several pairs of points and use the average of these values for a. The values for b were also calculated for each point and the average used in the equation.

ACCURACY OF CONDUCTOMETRIC METHODS.   The
relative change in the conductivity during the titration
mainly determines the accuracy of the titration.   The
presence of any foreign electrolytes which contribute to
the conductivity of the solution, therefore, decreases
the accuracy of the titration.   This does not preclude
the use of conductometric methods for solutions which
contain relatively large amounts of electrolytes, but for
these solutions precision methods of measurement of the
conductivity and careful maintenance of a constant
temperature must be used (11, p.226).

The method presupposes no change in volume during
the titration so the titrating reagent must be 10 to 100
times more concentrated than the solution being titrated
(2, p.48), (11, p.226).   A volume change of five percent
in the course of a titration is usually assumed to be
negligible (5, p.653).   If the volume change is greater
than this the measured conductivity may be corrected by
multiplying by the ratio

$$\frac{\text{Total volume of solution in the cell}}{\text{Initial volume}}.$$

This correction is based upon the assumption that within
the range of concentrations used in a titration the
specific conductivity is directly proportional to concen-
tration (2, p.49).   For most salts the conductivity

increases about 2 to 2.5 percent for a 1° C rise in temperature.   For this reason the titrations must be carried out at a constant temperature (11, p.226).

The usefulness and accuracy of conductometric analysis when applied to precipitation or complex formation is dependent upon these facts: (a) errors in determination of conductance data; (b) solubility of the precipitate or stability of the complex; (c) speed of formation of the precipitate; (d) constant composition of the precipitate (11, p.229).   The solubility of the precipitate or dissociation of the complex should be less than 5% (18, p.176).

EXPERIMENTAL

DESCRIPTION OF APPARATUS. A dipping type conductivity cell was used. The platinum electrodes were approximately $1\frac{1}{2}$ cm. square and were spaced 1 cm. apart. The electrodes were coated with platinum black. A 400 ml Berzelius beaker was used as a reaction vessel. This was placed in a liter beaker filled with ice which served as a constant temperature bath. Mixing was accomplished by the use of an electric stirring motor. A thermometer was also suspended in the reaction vessel.

ELECTRICAL CIRCUIT. A simple Wheatstone bridge circuit was employed with the conductivity cell serving as one arm of the bridge. A Leeds and Northrup Kohlrausch slide wire and a Leeds and Northrup a.c. resistance box made up the other three arms of the bridge. A Leeds and Northrup 1000 cycle microphone hummer was used. For most of the work reported in this thesis earphones were used as a null-point detector. It was found impractical to make use of the end coils of the Kohlrausch slide wire when using the earphones since a sharp null-point could not be obtained. The use of the end coils merely spread the null-point over a larger section of the slide wire.

A NEW NULL-POINT DEVICE. A great deal of work has been done on null-point devices to replace the earphones usually employed in conductometric work.

Kohlrausch used a galvanometer in his early work but later used earphones. Many investigators made use of a.c. galvanometers (2, p.33). Earphones, when used in a quiet room, are more sensitive than the galvanometers. In recent years electronic devices have been developed to replace the earphone. Garman and Kinney have designed an electronic bridge balance indicator which they claim has a sensitivity equal to the best earphones (9, pp.318-319). In a later paper Garman describes a vacuum tube instrument which gives a meter reading which is a linear function of the resistance of the cell (8, pp.146-147). Electronic circuits using a "magic eye" for a null-point indicator have been used (13, p.613).

A cathode-ray oscillograph was used in the latter part of this work following a suggestion by Professor J. C. Decius that the oscillograph could be used as a null-point device in a Wheatstone bridge circuit. The instrument used was a DuMont Cathode-Ray Oscillograph, type 304. This instrument has an amplifying circuit which amplifies the input signal before it is applied to the deflection plates of the cathode-ray tube.

The results obtained with this instrument were very satisfactory. It was possible to use the end coils on the slide wire and reproduce the slide wire settings with the same precision possible with the earphones and no

end coils.   Since the end coils are each 4500 ohms and the slide wire 1000 ohms, the effect of placing the coils in the circuit is to effectively increase the length of the slide wire ten times.   The divisions on the scale then represent one tenth the resistance indicated by the same divisions when the end coils are omitted.   The cathode-ray oscillograph was about ten times more sensitive than the earphones used.

STANDARDIZATION OF SOLUTIONS.   The sodium fluoride solutions were made up from C.P. sodium fluoride and standardized by evaporating to dryness in platinum crucibles with sulfuric acid.   The sodium sulfate was then weighed.   The dilute sodium fluoride solutions were kept in glass bottles and showed very little change on standing for several months.   The concentrated sodium fluoride solution was kept in a wax lined bottle.

The zirconia content of the zirconyl chloride octahydrate was determined by dissolving samples in water and immediately precipitating with ammonium hydroxide. The precipitate was ignited to the oxide, ZrO_2, and weighed.

INSTRUMENT CHECK.   Several acid-base titrations were carried out during the course of this work as a check on the instrument.   The same volume of a standard base was taken each time and titrated with a standard acid.

The end points obtained deviated from the mean by 2.5 percent. These titrations were carried out using earphones for the null-point indicator. This, then, sets the limit of accuracy for titrations on this instrument to 2.5 percent.

DIRECT TITRATIONS.

TITRATION OF ZIRCONYL CHLORIDE SOLUTIONS. The first attempts to titrate zirconium with sodium fluoride were made on solutions of zirconyl chloride. Curves such as Figures 1 and 2 were obtained. The titration curve has two breaks. The first break, which is very sharp, was found to be due to the titration of the free acid by sodium fluoride. Solutions of zirconyl chloride hydrolize to give strongly acid solutions. The pH's of zirconyl chloride solutions have been found equal to that calculated for a 10 percent hydrolysis of the salt to hydrochloric acid over a wide range of concentrations (1, p.473). Schorstein (14, p.94) has shown that strong acids may be accurately titrated conductometrically with sodium fluoride solutions. The conductivity curves obtained from a sodium fluoride-acid titration strikingly resemble those obtained from an acid-base titration. The author accounts for his results by stating that
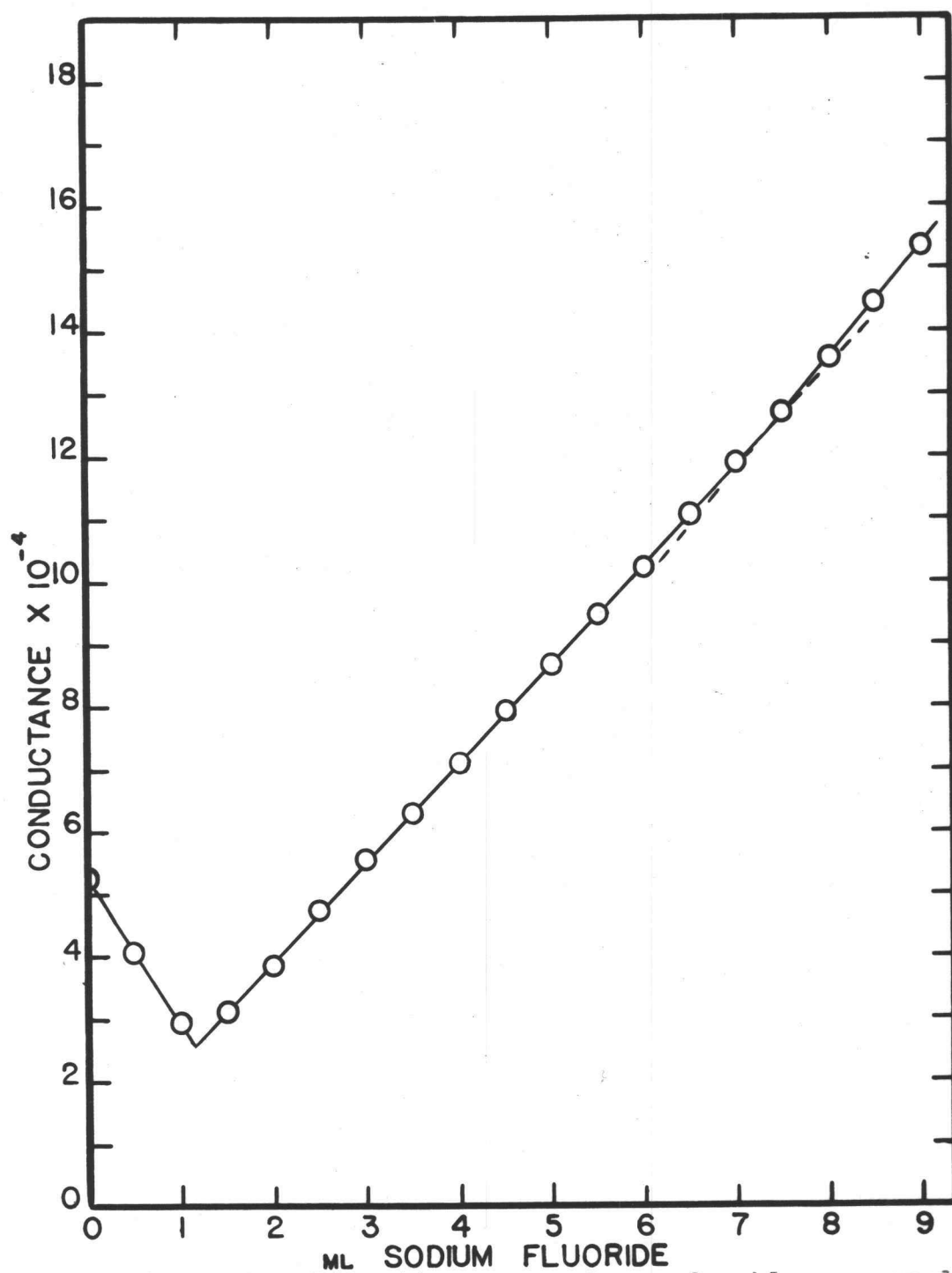
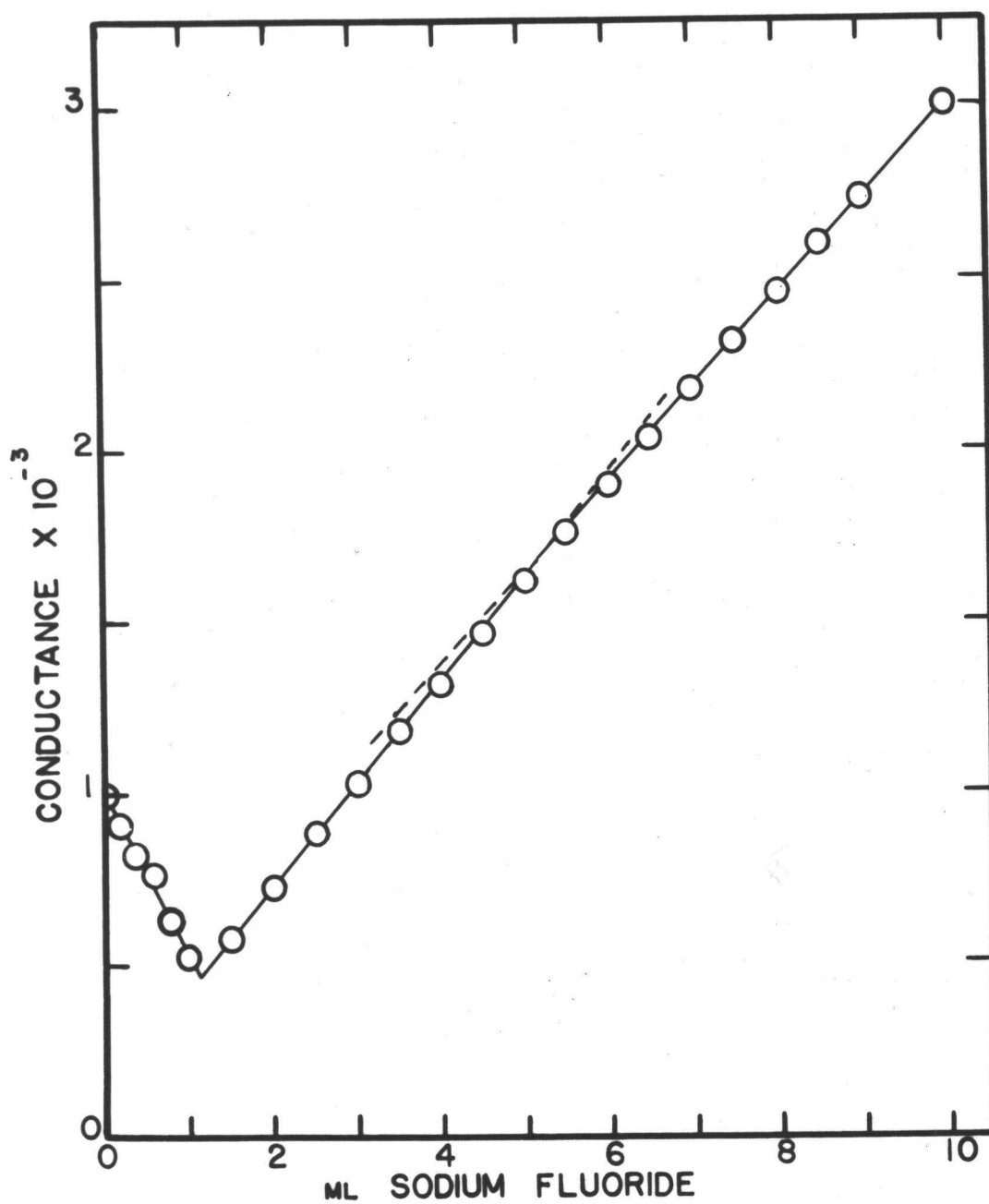Figure 1: Titration curve for a freshly prepared $ZrOCl_2$ solution.

Figure 2: Titration curve for a five day old
ZrOCl$_2$ solution.

slightly dissociated double salts of this general type NaCl·HF are formed (14, p.106). A more reasonable explanation of his results would be simply the removal of hydrogen ions from solution through the formation of slightly dissociated hydrofluoric acid.

The second break in the curve is due to the zirconium present. The break is not sharp enough to be of value in a analytical determination. If it is assumed that the zirconium possesses a coordination number of six in the complex formed, we can calculate the theoretical volume of sodium fluoride solution required to give a six to one ratio of fluoride to zirconium. For the titration represented by Figure 2 this volume was calculated to be 3.20 ml of sodium fluoride solution. From the titration curve the zirconium break is found at 5.00 ml. If we subtract from this the amount of sodium fluoride solution used to titrate the free acid, we will obtain the amount of sodium fluoride solution used to titrate the zirconium. This was found to be 3.85 ml of sodium fluoride solution as compared with the theoretical 3.20 ml. For the sample represented by Figure 1, the theoretical amount of sodium fluoride solution for a six to one fluoride to zirconium ratio is 3.27 ml. The amount used as determined from the curve was 6.00 ml.

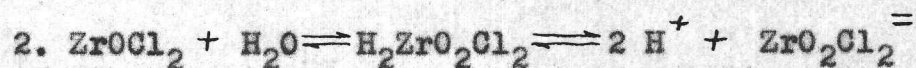The direction of the break in the conductivity

curve at the zirconium end point is of interest since it is dependent upon the age of the zirconyl chloride solution. Figure 1 represents the conductivity curve for a titration of a sample of this zirconyl chloride solution on the day the solution was made up. The titration represented by Figure 2 was made five days after the zirconyl chloride solution was made up. A further point of interest is the fact that the reaction between sodium fluoride solutions and the zirconyl chloride solutions was noticeably slow. The resistance of the cell would change slowly over a period of three to four minutes after the addition of reagent. This would indicate that the reaction taking place was not ionic.

Solutions of zirconium salts, especially the chloride, contain a large number of ionic species. Two equilibrium reactions which have been indicated to exist in zirconyl chloride solutions are:

1. $2ZrO^{++} + 4\ Cl^- + H_2O \rightleftharpoons Zr_2O_3^{++} + 4\ Cl^- + 2\ H^+$

and

2. $ZrOCl_2 + H_2O \rightleftharpoons H_2ZrO_2Cl_2 \rightleftharpoons 2\ H^+ + ZrO_2Cl_2^{=}$

Equilibrium conditions are reached slowly (1, p.473).

Since equilibrium is reached slowly there will be very little dichloro-zirconylic acid present when the solution is first made up. Presumably at this time the solution will contain largely chloride ions and zirconyl

ions.   The zirconyl ions are probably hydrated.   When
sodium fluoride is added to this solution the conductivity
increases.   This indicates that the complex formed by the
zirconium with the fluoride has a greater mobility than
the original zirconyl ion.   This would be reasonable if
the zirconyl ion had some water molecules coordinated to
it which would be replaced by fluoride ions to give a more
compact and, hence, a more mobile ion.   After the
zirconium end point has been reached the conductivity
increases at a still greater rate since we are merely
adding a salt.

After the solution has stood for several days,
there should be more dichloro-zirconylic acid in the
solution.   If the concentration of dichloro-zirconylic
acid is great enough, the direction of the break in the
titration curve should be opposite to that obtained in the
titration of a fresh zirconyl chloride solution.   When
the dichloro-zirconylic acid reacts with fluoride,
chloride ions will be released to the solution.   Since
the chloride ion is more mobile than the fluoride ion,
the conductivity of the solution will not increase as
rapidly after the zirconium end point as it does before.

TITRATION OF ZIRCONIUM SULFATE SOLUTIONS.   In an
attempt to nullify the change in zirconyl chloride
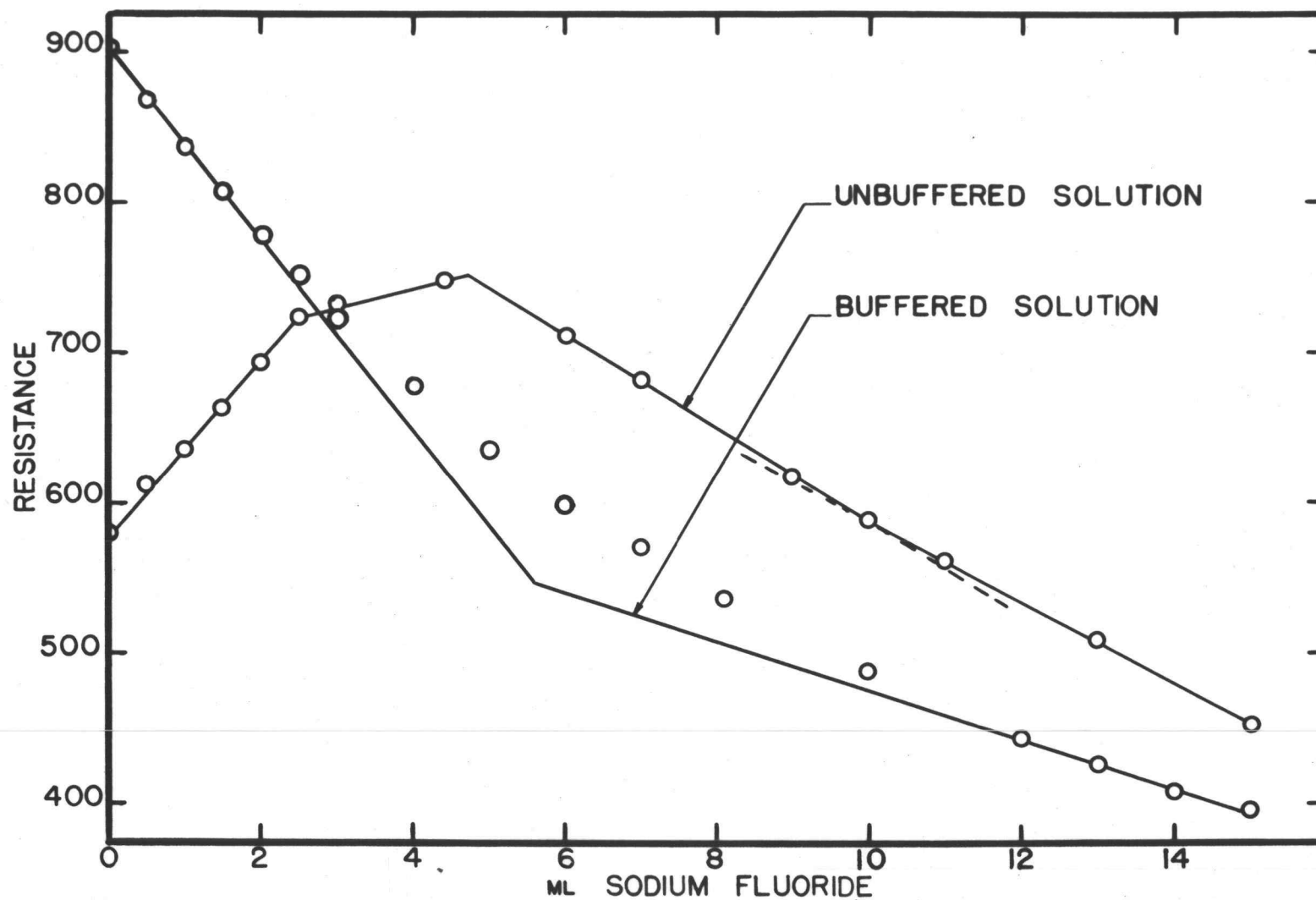solutions upon standing, samples of the solution were

Figure 3:   Titration curves for $Zr(SO_4)_2$ solutions.

taken and evaporated to near dryness with sulfuric acid.
These samples were then redissolved in water and titrated.
Titration curves such as the curve labeled unbuffered
solution, Figure 3, were obtained.   The first two breaks
in this curve are due to the two hydrogen ions of the
sulfuric acid.   The zirconium end point is again very
indistinct.   Strong acid solutions can not be used for
accurate titrations of zirconium for two reasons (1) the
break at the zirconium end point is not distinct and (2)
too much fluoride solution is used in titrating the acid
so that dilution errors become important.

Samples were then taken and evaporated to dryness
with sulfuric acid.   These were dissolved in water with
difficulty.   Some left an insoluble residue.   When first
dissolved the sulfate gave a clear solution which became
opalescent upon standing two to three minutes.   Titration
curves similar to that for the unbuffered zirconium
sulfate solution on Figure 3 were obtained.   This
indicates that not all of the sulfuric acid was removed by
evaporation.   According to Venable (17, p.77)
temperatures between 350-400° C. must be used to remove
all the sulfuric acid from the sulfate.   The temperature
of the hot plate used was found to be approximately
230° C.

To see if a weak acid such as acetic acid would

prevent hydrolysis of the zirconium sulfate solution,
several samples were dissolved by adding 0.1 to 0.2 ml of
glacial acetic acid to the sample and then dissolving in
water.   Clear solutions which showed no cloudiness on
standing overnight were obtained.   However, the stability
of these solutions was probably based on the formation of
diacetato-zirconylic acid, $H_2ZrO_2(C_2H_3O_2)_2$ (1, p.474),
rather than on the acidity of the solution.   The
possibility of carrying out the titration of the sulfate
in a buffered solution was next investigated.

TITRATIONS IN BUFFERED SOLUTIONS.

CHOICE OF BUFFER SYSTEM.   The characteristics
desired in the buffer system were an acid capable of hold-
ing the zirconium in solution and weak enough that it
would not react with the sodium fluoride.   Figure 4 shows
the curves obtained when tartaric, oxalic, and acetic
acids were titrated with sodium fluoride.   From the
curves it can be seen that tartaric and oxalic acid react
appreciably with sodium fluoride.   The acetic acid curve
shows a slight reaction at the start of the titration.
The fourth curve on Figure 4 represents the titration of
an acetic acid-sodium acetate mixture.   The straight line
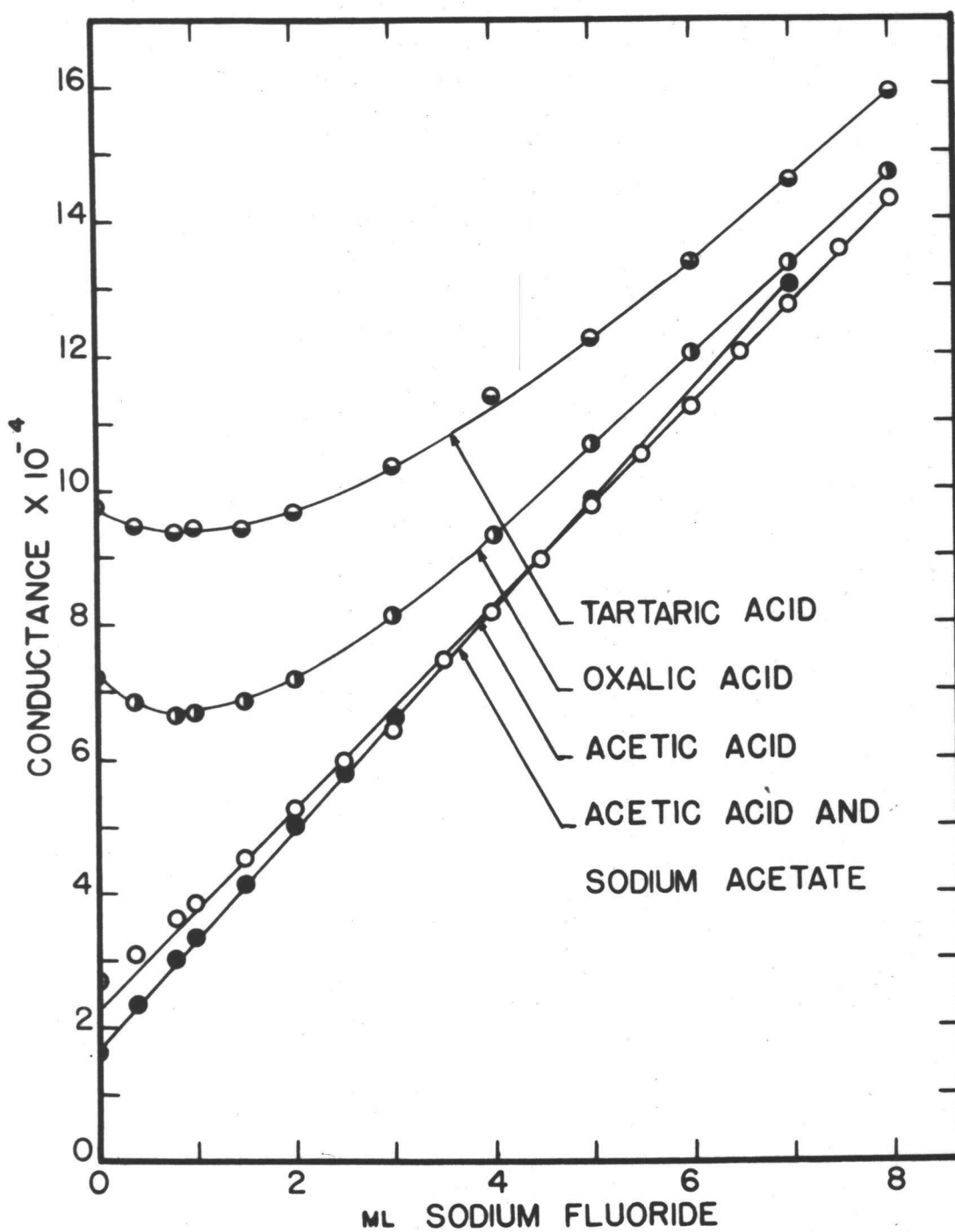obtained indicates that the sodium fluoride does not react

Figure 4: Titration curves for some organic acids.

with the acetic acid in the buffer solution. The
ionization of the acid is repressed by the acetate
sufficiently to prevent reaction. Potassium acid
phthalate was also tried but gave titration curves similar
to those for tartaric acid and oxalic acid; in addition,
a precipitate of phthalic acid was formed by the inter-
action of the acid salt and sulfuric acid when used to
buffer a zirconium sulfate sample. On the basis of these
curves and the fact that acetic acid solutions of
zirconium were stable, it was decided to use an acetic
acid-sodium acetate buffered solution in the titration.

TITRATION PROCEDURE. Aliquots of a standard
zirconyl chloride solution were taken and evaporated to
dryness with sulfuric acid in a beaker. These were then
dissolved by adding 0.1 to 0.2 ml of glacial acetic acid,
depending upon the size of the sample, and about 25 ml of
water. If the sample did not go into solution
immediately the beaker was warmed a few minutes on the hot
plate until a clear solution was obtained. To the clear
solution was added 0.5 to 1.0 ml of 3N sodium acetate.
The solutions were then transferred to the Berzelius
beaker and diluted with cold distilled water to 200 or 300
ml depending upon the size of the sample. The distilled
water used for diluting the samples was precooled in an
icebath. The Berzelius beaker was placed in the icebath,

the stirring motor turned on, and the solution was allowed to stand until a constant temperature was reached. The titration was then carried out by adding portions of sodium fluoride solution and recording the resistance of the cell after each successive addition of reagent. Carefully weighed amounts of zirconyl chloride octahydrate were used for the larger samples. These were dissolved in a small amount of water and then evaporated to dryness with sulfuric acid.

The amount of sodium acetate needed to buffer the sulfuric acid which remained in the sulfate residue was determined experimentally. For the samples containing 7 to 14 milligrams of zirconium it was found that 0.5 ml of the 3N sodium acetate solution was required. If an insufficient amount of buffer is used the first part of the titration curve will be irregular. The first portion of the titration curve of a properly buffered solution is a straight line. An insufficient amount of sodium acetate is readily detected from the shape of the initial portion of the titration curve. A fairly large excess of buffer can be used. A very large excess of sodium acetate is not desired since it increases the conductivity of the solution and thereby reduces the sensitivity of the titration. One milliliter of the sodium acetate solution was found to be adequate for any of the samples titrated.

The type of titration curve obtained for these solutions is illustrated by the second curve on Figure 3. The sample represented by this curve contained 0.0144 gram of zirconium. It is to be noticed that the angle between the two lines in this case is much sharper than that in the case of the unbuffered solution. If the zirconium is present in this solution as the acetate or diacetato-zirconylic acid rather than as the sulfate, such an increase in the sharpness of this break would be expected. The replacement of acetate ions bound to the zirconium atom by fluoride would cause a greater change in the con-ductivity than would the replacement of sulfate ions by fluoride. This greater change in conductivity results in a sharper break at the end point.

ANALYTICAL RESULTS. Table 1 lists the results of several titrations employing acetic acid-sodium acetate solutions. As can be seen from the table the end points are not very reproducible. The weight of zirconium found was calculated on the assumption of a coordination number of six for the complex formed. The results are very poor. Since the errors are in both directions the use of a different coordination number would reduce the errors in one direction while increasing the errors in the other direction.

Figure 5 is the titration curve for sample 10 of

TABLE I

ANALYTICAL RESULTS

Sample Number	Weight Zr taken grams	Titer NaF ml	Weight Zr found grams	Percent error
1	0.0072	4.17[1]	0.0092	+27
2	0.0072	4.22[1]	0.0093	+29
3	0.0072	4.04[1]	0.0089	+23
4	0.0072	4.28[1]	0.0094	+31
5	0.0144	6.12[1]	0.0135	−6
6	0.0144	5.60[1]	0.0123	−15
7	0.0362	6.15[2]	0.0277	−23
8	0.0364	5.74[2]	0.0258	−29
9	0.0723	5.95[3]	0.0783	+8
10	0.0725	6.00[3]	0.0789	+9

[1] Sodium fluoride solution number 1 − 0.000145 mole NaF per ml
[2]   "   "   "   "   2 − 0.000296 "   "   "   "
[3]   "   "   "   "   3 − 0.000865 "   "   "   "
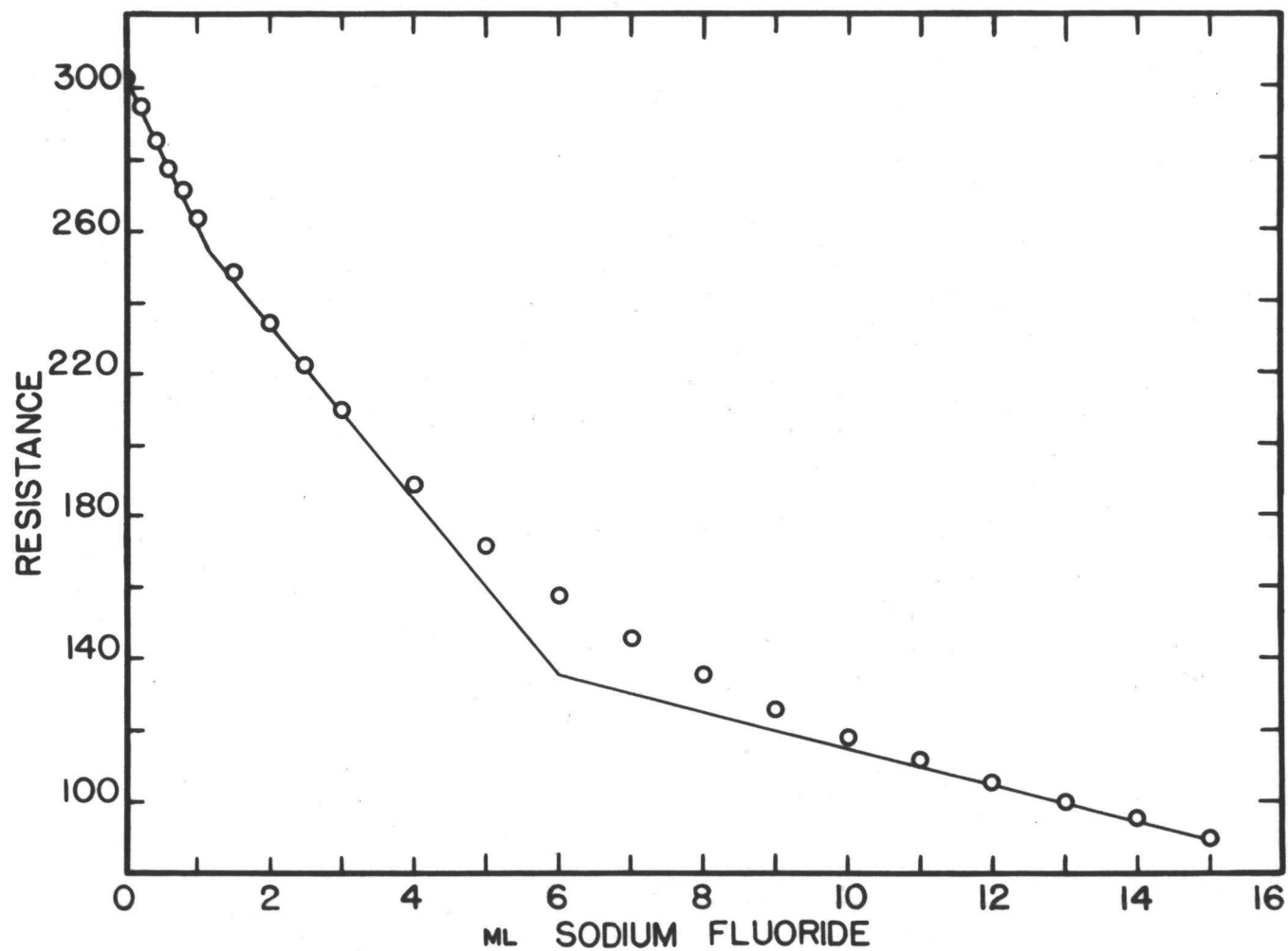
Figure 5: Titration curve for a buffered $Zr(SO_4)_2$ solution.

Table 1. This may help to explain the poor results obtained in the titrations. The first break in the curve occurs at 1.20 ml. At this point we have a fluoride to zirconium mole ratio of 1.3:1. This initial break does not appear in the titration curves for samples 1 through 6 since it would take place in the first 0.1 to 0.2 ml of the titration for these small samples. The fluoride to zirconium ratios at this initial break for samples 7, 8 and 9 are, respectively, 0.75:1, 0.82:1, 1.3:1. Apparently the formation of the fluoride complex of zirconium proceeds by a stepwise process, with the fluoride ions entering the complex one at a time. There is probably some overlapping in the process which results in the rounded portion of the titration curve. The straight sections of the titration curves are not long enough for extrapolation to an accurate end point

OTHER EXPLORATORY EXPERIMENTS. Several other titrations were attempted. None of these showed any promise of being developed into an analytical procedure.

Zirconyl chloride solutions were titrated after being buffered with sodium acetate. The plot of volume of titrant vs. conductance yielded a straight line. The addition of sodium acetate lowered the pH of the solution to the point where the zirconium hydrolized to such an extent that it could not react with the fluoride ion.

The fluoride titration was reversed. A measured amount of the standard fluoride solution was placed in the reaction beaker and titrated with a zirconium solution. The zirconium sample was evaporated to dryness with sulfuric acid, dissolved and buffered in the usual way, and made up to volume in a volumetric flask. The resulting titration curve was a straight line up to a point near the calculated equivalence point (for a 6:1 mole ratio of fluoride to zirconium) after which it was a rather irregular curve. The solution was milky at the end of the titration. The zirconium added after the fluoride was used up hydrolized.

An excess of fluoride solution was added to a zirconium sample and the excess fluoride was titrated with thorium nitrate. The results of this titration indicated that the thorium was stripping the fluoride from the zirconium complex.

SUMMARY

An attempt has been made to develop a conductometric titration of zirconium using a fluoride solution as a complexing reagent. The method has been shown to be impractical.

Titration curves for some zirconium solutions have been presented and their significance discussed.

The study indicates that conductivity measurements could be used to advantage in studying the nature of the zirconium ion in solution.

A cathode ray oscillograph was used as an end point device in part of this work, and was found to be ten times more sensitive than the earphones used.

LITERATURE CITED

1. Blumenthal, Warren B. Some features of zirconium chemistry. Journal of chemical education 26:472-475. 1949.

2. Britton, Hubert T. S. Conductometric analysis. New York, D. Van Nostrand, 1934. 178p.

3. Claassen, A. Die massanalytische und gewichts-analytische Bestimmung von Zirkon und Hafnium, einzeln und auch nebeneinander, mit seleniger Säure. Zeitschrift für analytische Chemie 117:252-261. 1939.

4. Connick, R. E. and W. H. McVey. The aqueous chemistry of zirconium. Oak Ridge, Tennessee, Technical information division, Oak Ridge directed operations. 1948. 57p. (United States atomic energy commission AECD - 2272)

5. Corwin, J. F., A. P. Dresel, and G. E. Osuch. Conductometric titrations with organic reagents. Analytical chemistry 22:653-654. 1950.

6. Corwin, J. F. and H. V. Moyer. Conductometric titrations with organic reagents. Industrial and engineering chemistry, analytical edition 18:302-304. 1946.

7. Furman, N. Howell. Electrotitrations. Transactions of the electrochemical society 76:45-61. 1939.

8. Garman, R. L. A continuous-reading electron-tube conductance meter. Industrial and engineering chemistry, analytical edition 8:146-147. 1936.

9. Garman, R. L. and G. F. Kinney. An electronic bridge balance indicator for conductance measurements. Industrial and engineering chemistry, analytical edition 7:318-319. 1935.

10. Harned, Herbert S. The titration of some bivalent metal sulfates by the conductance method. Journal of the American chemical society 39:252-266. 1917.

11. Kolthoff, I. M. Conductometric titrations.
    Industrial and engineering chemistry,
    analytical edition 2:225-230. 1930.

12. Kumins, Charles A. Zirconium determination in presence
    of interfering elements. Analytical chemistry
    19:376-377. 1947.

13. Müller, Ralph Holcombe. American apparatus,
    instruments, and instrumentation. Industrial
    and engineering chemistry, analytical edition
    12:571-630. 1940.

14. Schorstein, Herbert. Die konduktometrische Verfolgung
    der Reaktionen des Fluorions und ihre Anwendung
    auf bodenkundliche Probleme. Bodenkunde und
    Pflanzenernährung 3:89-107. 1937.

15. Simpson, Stephen G. and Walter C. Schumb. The
    selenious acid method for the determination of
    zirconium. Journal of the American chemical
    society 54:921-933. 1931.

16. van Suchtelen, F. H. Hesselink and Arao Itano. The
    electro-titrametric method and its application
    to general analytical chemistry. Journal of the
    American chemical society 36:1793-1803. 1914.

17. Venable, Francis P. Zirconium and its compounds.
    New York, Chemical catalog co., 1922. 173p.
    (American chemical society monograph series
    no. 5)

18. Willard, Hobart H., Lynne L. Merritt Jr., and John A.
    Dean. Instrumental methods of analysis. New
    York, D. Van Nostrand, 1948. 247p.

19. Zolotukin, V. K. Determination of zirconium by the
    acidimetric method with hydroxy compounds.
    Chemical abstracts 36:1263. 1942.