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Determination of Chloride in Zirconium Metal

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Abstract: Zirconium metal is dissolved in a mixture of H_2SO_4 - HF acids and the chloride ion in the range of 5-250 ppm is determined by an automatic potentiometric titration with $AgNO_3$.

Introduction: Due to its physical, chemical, and nuclear properties, zirconium metal has become an important element in the reactor development program. Minor impurities in this metal greatly affect its chemical and physical properties. Zirconium metal containing chlorides is thought to be more susceptible to corrosion than chloride-free metal. Therefore, it became necessary to determine small amounts of chloride in zirconium.

It has been reported by C. J. Rodden[1] that chloride has been determined by a nephelometric procedure. However, it was believed that a precise volumetric method, if it could be extended to the range of 5-50 micrograms of chloride, would be preferable.

Experimental: Standard solutions of 0.1 N NaCl and 0.1 N $AgNO_3$ were made with reagent grade chemicals and standardized gravimetrically according to the method of Kolthoff and Sandell[2]. Dilutions of these solutions were made to give 0.01 N solutions. The 0.01 N $AgNO_3$ was used as the titrant and 100 λ aliquots of the 0.01 N NaCl were titrated as standards.

A Dow Recordomatic Titrator[3] that originally came equipped with 50 ml syringe burets was fitted with a 0.5 ml syringe buret. This buret, by calibration with known chloride solutions, was found to give uniform delivery of the 0.01 N $AgNO_3$ solution. As the syringe buret is directly coupled to the chart of the recorder by a system of gears, the chart travel is a positive measure of the volume of titrant added. Also, the titrant is

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fed only when the system is in equilibrium, as a sudden change of potential of only two millivolts will automatically stop the buret and chart. Thus, as the equivalence-point is approached, the addition of the titrant is limited to a very small increment. A typical titration curve is shown in Figure 1. The mid-point of the break in potential is taken as the equivalence-point. The inches of chart travel from the start of the titration to this point is a measure of the chloride ion.

A 20 ml beaker was made from polystyrene and used as the titrating vessel. This was placed in a methyl alcohol-dry ice bath to maintain the titrating temperature of 4°-10° C. An iron bar 1/8" in diameter and 3/4" long was enclosed in "teflon" and used as a magnetic stirring bar. The electrode system consisted of a 6" length of No. 18 pure silver wire as an indicating electrode[4]; a Beckman No. 4970 Calomel electrode, connected to the titrating solution with a KNO_3-Agar salt bridge enclosed in tygon tubing, served as the reference electrode. A drawing of the electrode assembly is shown in Figure 2.

One hundred lambda aliquots of the 0.01 N NaCl were carefully pipetted into the plastic beaker and the volume was made up to 5 ml with distilled water. Five drops of concentrated HNO_3 were added, and the solution cooled to 4°-10° C before titration. The results of six titrations are shown in Table I.

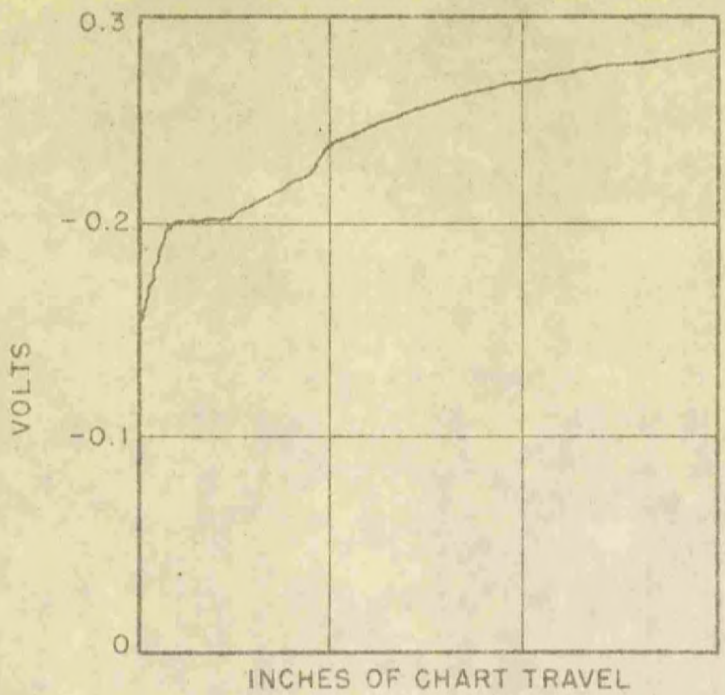

FIG. 1
CHLORIDE IN ZIRCONIUM METAL TITRATION CURVE

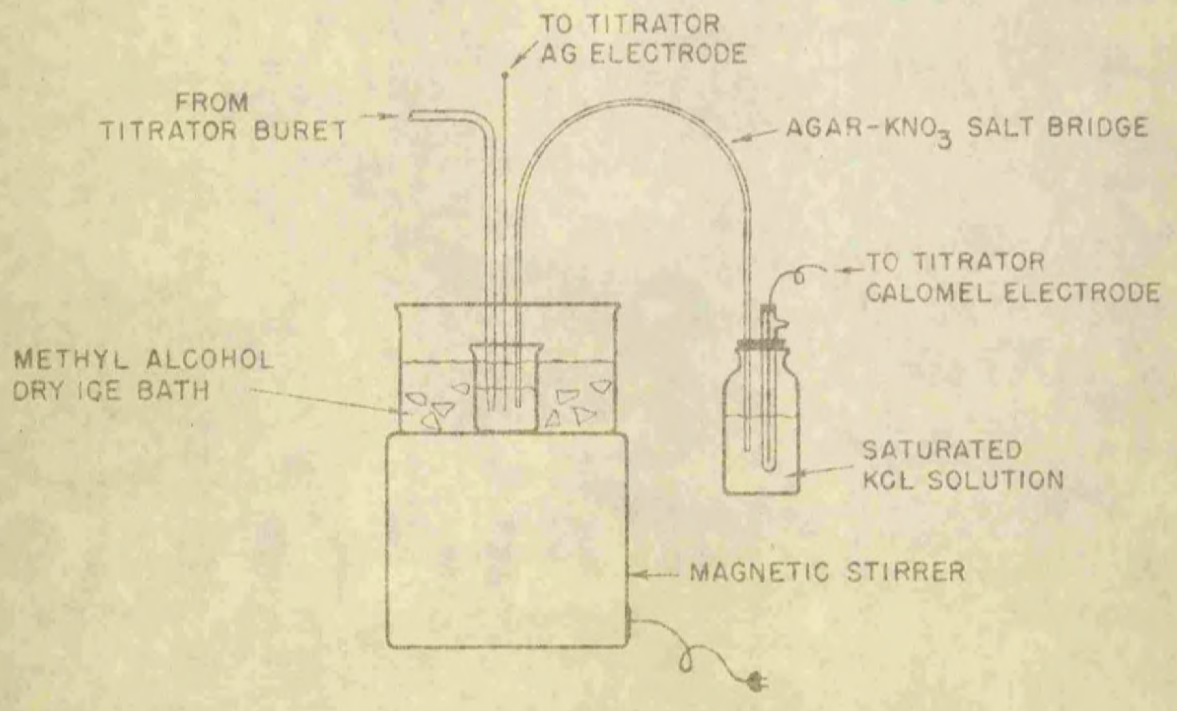

FIG. 2
ELECTRODE ASSEMBLY

Table I

Titration of 100 Aliquots of 0.01 N NaCl (35.45 γ Cl^-)

Number	Inches of Chart Travel	% Deviation from Average
1	3.45	-2.0
2	3.50	-0.3
3	3.55	+1.7
4	3.50	-0.3
5	3.50	-0.3
6	3.55	+1.7

Average 3.51" (1 inch of chart equals 10.16 γ Cl^-).

It can be seen from this table that the chloride ion may be titrated in the desired range.

One gram samples of NBL 284 zirconium metal were dissolved in a mixture of 0.5 ml concentrated H_2SO_4, 1 ml of 42% HF, and 5 ml of distilled water using plastic beakers. It was found that the use of glass beakers led to high results, probably due to the dissolving of chloride from the glass by the HF. Therefore, glass surfaces in contact with the solutions were held to a minimum. Several 1 g samples of NBl 284 gave erratic results ranging from 9 γ to 20 γ of Cl^- per gram of metal. It was believed that the inconsistency was caused by inhomogeneity of the sample. A 10 gram sample therefore, was dissolved in a plastic beaker as before, and the volume adjusted to 50 ml with distilled water. Five ml aliquots containing one gram of zirconium were then titrated. Blanks of the reagents gave a very small titration correction. A spike of 9 γ Cl^- was added to two of the 5 ml aliquots. The results are shown in Table II.

Table II

Chloride Found in 1 Gram of NBL 284 Zirconium Metal

Number	Inches of Chart Travel	γ Cl^- Found
1	0.90	9.1
2	0.90	9.1
3	0.90	9.1
4	0.95	9.6
5*	0.90	9.1
6*	1.70	17.3 - 9.0γ Cl^- spike = 8.3γ
7*	1.75	17.8 - 9.0γ Cl^- spike = 8.8γ

Average 9.0 γ Cl^-/g Zr = 9 ppm of Cl^-.
6* and 7* contained 9 γ Cl^- spike.

This table shows that the titration is quite reproducible and that a relatively large sample of the metal should be dissolved in order to lessen the difficulties due to the inhomogeneity of small samples.

A number of zirconium samples have been submitted by Mr. A. R. Olsen of the Reactor Technology Division and have been analyzed by this method. The results of duplicate samples are shown in Table III.

Table III

Analysis of Various Zirconium Samples

Sample No.	PPM Chloride Found
IR-6	42
IR-6	45
VI-D outside	27
VI-D outside	25
VI-D center	22
VI-D center	15

Summary: An automatic potentiometric titration method for the estimation of chlorides in zirconium metal has been presented. It is capable of determining as low as 5 ppm of chloride using a one gram sample.

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1. Rodden, C. J., Minutes of Zirconium Conference US AEC New Brunswick Laboratory, New Brunswick, N. J., NYOO-2005.

2. Kolthoff, I. M., and Sandell, E. B., Quantitative Inorganic Analysis, MacMillan Company, New York N. Y., 1943, p. 311.

3. Dow Recordomatic Titrator obtained from Precision Scientific Company, 3737 W. Cortland St., Chicago 47, Ill.

4. Kolthoff, I. M., and Furman, N. H., Potentiometric Titrations, John Wiley and Sons, Inc., New York, N. Y. 1931, p. 144.

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