

ENGINEERING RESEARCH INSTITUTE  
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PROGRESS REPORT

APPLICATION OF THE POLAROGRAPH TO ANALYSIS  
OF TITANIUM-BASE ALLOYS

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## APPLICATION OF THE POLAROGRAPH TO ANALYSIS

## OF TITANIUM-BASE ALLOYS

SUMMARY

The present report covers the period from October 7 to December 7, 1952. During this period, ferric and chromic ions were studied polarographically in the presence of titanous ion. Potassium fluoride was employed as the supporting electrolyte in all these solutions, since titanium metal and titanium-base alloys can be dissolved easily in hydrofluoric acid. In addition, ferric and chromic ions seem to have well-defined waves in fluoride medium under the right pH condition.

SUMMARY OF RESULTSA. Preliminary Investigation

Heyrovsky<sup>1</sup> found the half-wave potential,  $E_{1/2}$ , for  $Fe^{+3}$  in 0.1 M  $KHF_2$  solution to be about -0.6 v versus the saturated calomel electrode; in a similar medium, Zuman<sup>2</sup> found  $E_{1/2}$  to be -0.57 v. We have found  $E_{1/2}$  for  $Fe^{+3}$  in a KF solution (ca. 0.3 M) at a pH of 5.0 to be -0.57 v. However, we also observed that  $E_{1/2}$  for  $Fe^{+3}$  in a 0.5 M KF solution adjusted to pH 6 with KOH is -1.35 v. The latter value agrees with that of Stackelberg and Freyhold<sup>3</sup>, who reported that  $Fe^{+3}$  produced a reduction wave with  $E_{1/2}$  of -1.36 v which remained constant when the concentration of KF was increased from 0.04 to 0.8 M. The pH's of their solutions were not specified. On the other hand, West and Dean<sup>4</sup>, using a 1 M NaF supporting electrolyte in the range of 4 to 7 containing 0.004% gelatin, claimed to have found no reduction wave for  $Fe^{+3}$  prior to the discharge of sodium ion.

Kolthoff and Lingane<sup>5</sup> suggest the differences in pH as an explanation for these discrepancies. Apparently,  $E_{1/2}$  is a critical function of pH; however, the possibility of decrease or of complete obliteration of the wave due to the strong ferric-fluoride complex is a more logical explanation. The ferric-ferrous-fluoride system has been investigated<sup>6</sup>; the stability constant for the ferric-fluoride complex was found to be  $10^{12}$  while that of the ferrous-fluoride complex was less than 30.

We also find that a concentration of less than about 1.5% (0.3 M) fluoride is insufficient to hold  $Fe^{+3}$  in solution when the pH is increased above 3 but not higher than 7. It is hardly possible to work with fluoride solution in glass apparatus below a pH of 5.

### B. Experimental Procedure

In studying the polarograms of pure  $Fe^{+3}$  and  $Cr^{+3}$  ions, standard solutions of  $FeCl_3$  and  $K_2CrO_7$  were diluted with 0.5 M KF solution to make approximately 0.5 mM solutions. Then 50% KOH solution was added to adjust the pH to between 6 and 7. In the case of dichromate, a 1% solution of  $NH_4HSO_3$  was added to reduce the  $Cr^{+6}$  to  $Cr^{+3}$ , since the chromate waves are not entirely satisfactory for polarographic analysis.

In this medium  $Fe^{+3}$  was found to have an  $E_{1/2}$  of -1.35 v and  $Cr^{+3}$   $E_{1/2}$  of about -1.65. A mixture of  $Cr^{+3}$  and  $Fe^{+3}$  was then studied in 0.5 M KF solution, where it was found that the two waves could be distinguished. In these solutions, the  $NH_4HSO_3$  does not affect the  $Fe^{+3}$ , for the latter is tightly bound in its fluoride complex.

### C. Separation of Titanium as $K_2TiF_6$

The experiment of the previous section were then repeated with the introduction of titanic ion. Samples of pure  $TiO_2$  (0.4 to 0.8 g.) were dissolved in concentrated hydrofluoric acid and the same amounts of  $Fe^{+3}$  and  $Cr^{+6}$  were added. The  $Cr^{+6}$  was reduced to  $Cr^{+3}$  with  $NH_4HSO_3$  and the excess bisulfite was removed by boiling the solution. The latter was concentrated to about 3 ml. In order to obtain suitable waves for  $Fe^{+3}$  and  $Cr^{+3}$ , the majority of the  $Ti^{+4}$  must be removed, allowing us to use a higher sensitivity when recording a polarogram. The presence of a large excess of  $Ti^{+4}$  produces a large current which makes the precise measurement of the normal  $Fe^{+3}$  and  $Cr^{+3}$  currents practically impossible. The method used for removing titanium was based on that of Noyes and Bray<sup>7</sup>. The flow sheet diagram of Fig. 1 illustrates the process.

The resulting polarograms indicated nearly quantitative removal of  $Ti^{+4}$ , but the  $Cr^{+3}$  wave was also lacking. The  $Fe^{+3}$  wave was still observed, however.

Since the  $\text{Cr}^{+3}$  wave appears at a very negative potential (-1.65 v) and  $\text{K}^+$  ion discharges somewhat before -2 v, it was desirable to separate these waves further. The use of  $\text{Li}_2\text{CO}_3$  instead of  $\text{K}_2\text{CO}_3$  to neutralize the hydrofluoric acid seemed to be a possible answer, since  $\text{Li}^+$  ion has a more negative  $E_{1/2}$  value than  $\text{K}^+$  ion. However,  $\text{LiF}$  is so extremely insoluble that  $\text{Li}^+$  ion could not be used.

In another variation, 99.99% titanium metal, secured from the Foote Mineral Company was used and solutions were prepared by dissolving pure titanium, iron, and chromium metals in hydrofluoric acid and oxidizing the metals to  $\text{Ti}^{+4}$ ,  $\text{Fe}^{+3}$ , and  $\text{Cr}^{+6}$  respectively with persulfate and a trace of  $\text{Ag}^+$ . The excess persulfate was removed by boiling the solution, and then the solution was treated as in Fig. 1.

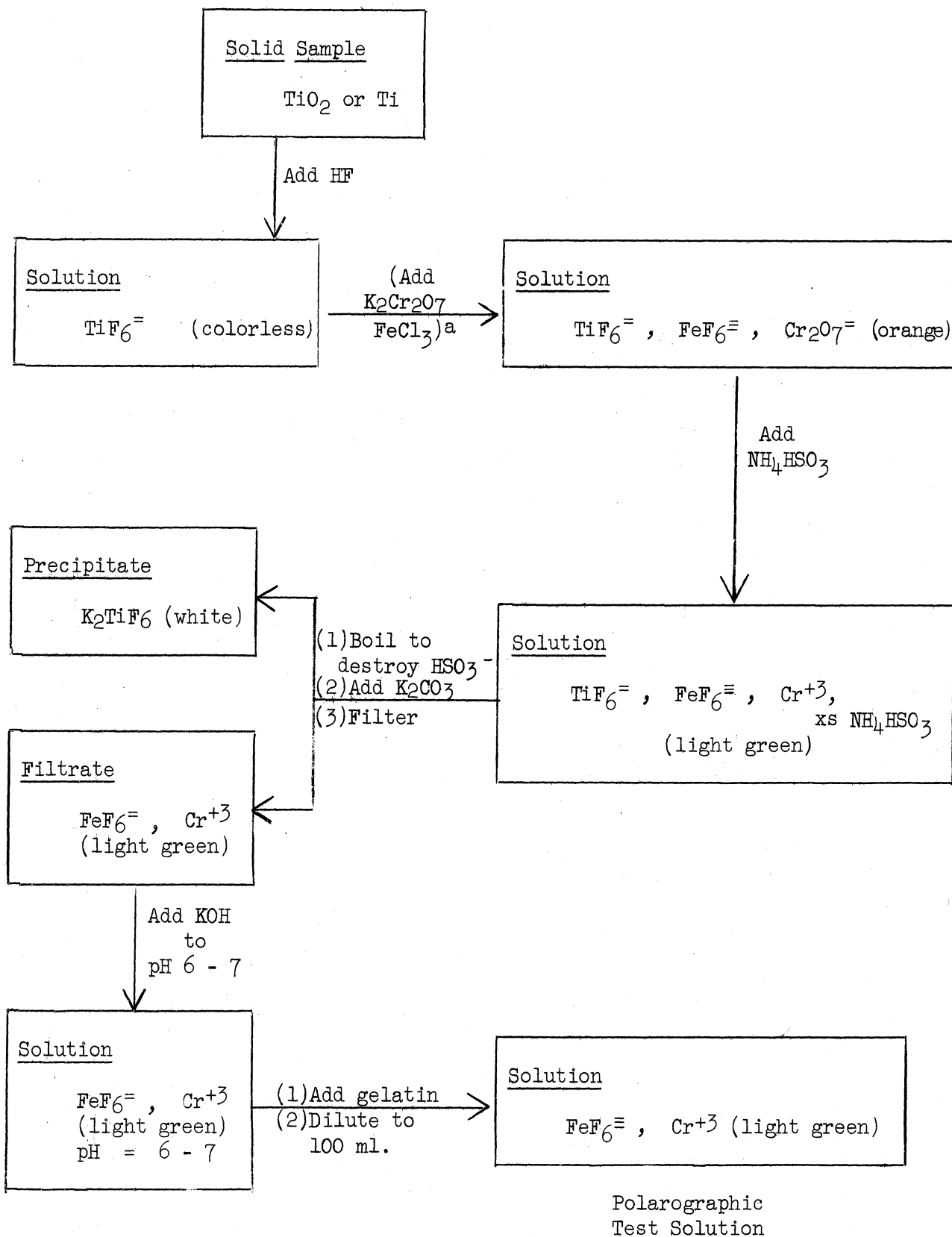
#### D. Polarographic Studies of $\text{Cr}^{+3}$ and $\text{Fe}^{+3}$ After $\text{Ti}^{+4}$ Removal

The filtrates from the previous separations were studied polarographically and many curious but, unfortunately, undesirable phenomena were observed. The first major trouble was the irregular drop-time observed for the dropping mercury electrode. As the applied potential is increased to more negative values, the drop-time increases until the mercury flow ultimately becomes a stream, and the current drops nearly to zero. This effect was somewhat overcome by the addition of gelatin, but the effect varies with each solution, so a further control of variables is necessary. This irregular drop-time has been observed with four different capillaries.

Most of these solutions possessed a hydrogen wave which completely obliterated the  $\text{Fe}^{+3}$  and  $\text{Cr}^{+3}$  waves. The reason for the nonreproducible phenomena sometimes observed after removal of  $\text{Ti}^{+4}$  may be attributable to a rather poor procedure of controlling the variables. Since the sample is dissolved in concentrated hydrofluoric acid (27 M) and then concentrated to a small volume, the amount of fluoride ion present varies from sample to sample. The amount of  $\text{K}_2\text{CO}_3$  necessary therefore varies with the samples. Also the final pH adjustment with KOH requires different amounts of KOH for each sample, which means that final solutions contain variable amounts of both fluoride and potassium ion. A better control over these variables is essential and will be maintained in the future.

#### FUTURE WORK

A systematic independent study of chromic and ferric ions with respect to pH, concentration of fluoride ion, and other environmental and



<sup>a</sup> The iron and chromium would be present in an actual sample.

Figure 1. Preparation of Low-Titanium-Content Polarographic Solution.

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experimental variables is necessary in order to obtain a standard optimum set of conditions for further work. We have not, of course, abandoned the possibility of there being a more suitable supporting electrolyte than fluoride ion. We still propose to study this system in other media such as tartarate, citrate, etc.

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