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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 February 7, 1953, to April 7, 1953. During this period, two separate lines of investigation were followed. One study involved the simultaneous determination of chromium and iron in alkaline cyanide solution; initial application of the procedure to a known titanium sample gave satisfactory chromium results but high iron results. The cause of the latter is being checked. The other area of study is concerned with the amperometric titration of vanadium in a solution of the type that would occur during the iron-chromium procedure mentioned.

SUMMARY OF RESULTSA. Simultaneous Determination of Chromium and Iron

The chromium system was first studied in potassium fluoride medium. Both chromic and chromate ions were investigated, and it was found that neither of these forms gave a reduction wave in the presence of potassium fluoride. It had been hoped that a reduction wave could be obtained for chromium in fluoride medium where a ferric iron reduction wave had been observed, so that both ions could be determined in the same medium. Since it was not possible to obtain a wave for chromium, it was necessary to study both ions in an entirely new system.

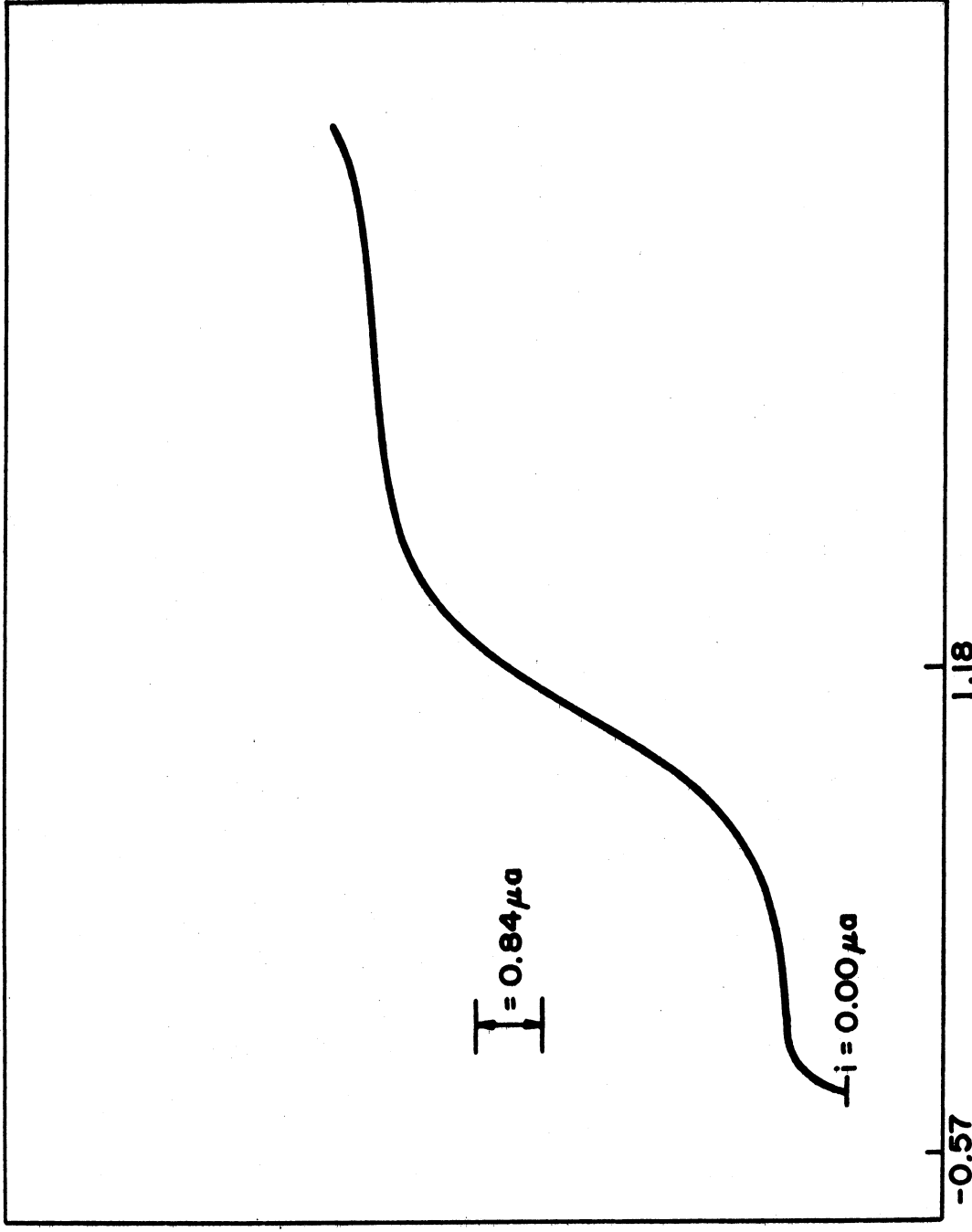
An alkaline cyanide system was suggested, since Lingane and Kolthoff<sup>1</sup> have reported suitable chromate reduction waves in 1.0 M KOH,

and the ferricyanide complex is stable enough to immobilize iron in strongly basic solution. Both ferric iron and chromate were studied in basic solutions of their pure salts, and it was found that the diffusion currents obtained for these ions were proportional to their respective concentrations. Since the ferricyanide reduction wave occurs at +0.2 volt vs. S.C.E. in 0.8 M KOH, where the anodic mercury cyanide wave is superimposed upon it, it was found necessary to measure the iron wave by measuring the residual current at approximately -0.6 volt, slightly more negative than the mercury cyanide wave. The  $E_{1/2}$  for the  $\text{CrO}_4^{-2} \rightarrow \text{Cr}^{-3}$  reduction was -1.05 volt vs. S.C.E. in 0.8 M KOH.

Titanium alloy samples of known composition containing small amounts of iron and chromium were obtained from Dr. John H. Enns of the Physics Department of the University of Michigan. Approximately 0.5-g samples were dissolved in 5 ml of 1:1 hydrofluoric acid containing 0.5 ml of concentrated nitric acid. The latter was added in order to oxidize any material which does not dissolve in the hydrofluoric acid and thus to facilitate solution of the sample. A 50% solution of potassium fluoride was then added dropwise until precipitation of  $\text{K}_2\text{TiF}_6$  was essentially complete (the recovery of titanium at this point is not quantitative). The precipitate was then filtered and washed with a solution which was 1% in hydrofluoric acid and 1% in potassium fluoride. The filtrate was collected in a platinum dish and, after the addition of about 5 ml of sulfuric acid, was concentrated by evaporation in order to remove most of the excess fluoride ion. The resulting solution was then transferred to a beaker, diluted to approximately 200 ml, and heated to boiling; the chromium was oxidized to chromate by the addition of one drop of 0.5 M silver nitrate solution and 3 g of ammonium persulfate. After the excess persulfate was removed by boiling, the solution was cooled and a solution of 8 g of potassium cyanide in 50 ml of concentrated ammonia was added to convert the ferric iron to the ferricyanide complex and at the same time to precipitate the remaining titanium as  $\text{Ti}(\text{OH})_4$ . The solution was once again filtered and the filtrate evaporated to about 50 ml. When the latter was cool, 2 ml of 1% gelatin solution was added and the solution was diluted to 250 ml with 1.0 M KOH solution. A polarogram of the resulting test solution was then recorded and compared with those of standard solutions of iron and chromium.

Other variations of the above method were tried for the removal of titanium but were found to give erroneous results. An attempt was made to remove all the titanium as  $\text{Ti}(\text{OH})_4$ , but the gelatinous precipitate formed was very difficult to filter, and occlusion of iron and chromium was very pronounced.

Figure 1 shows a typical polarogram of the iron and chromium system in 0.8 M KOH solution. As can be seen, both waves are well defined and the wave heights can be measured easily. Figure 2 shows the calibration



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FIG. 1. POLAROGRAM SHOWING CURVE FOR 1.117mg. Fe AND 1.73mg. Cr PER 100 ml.

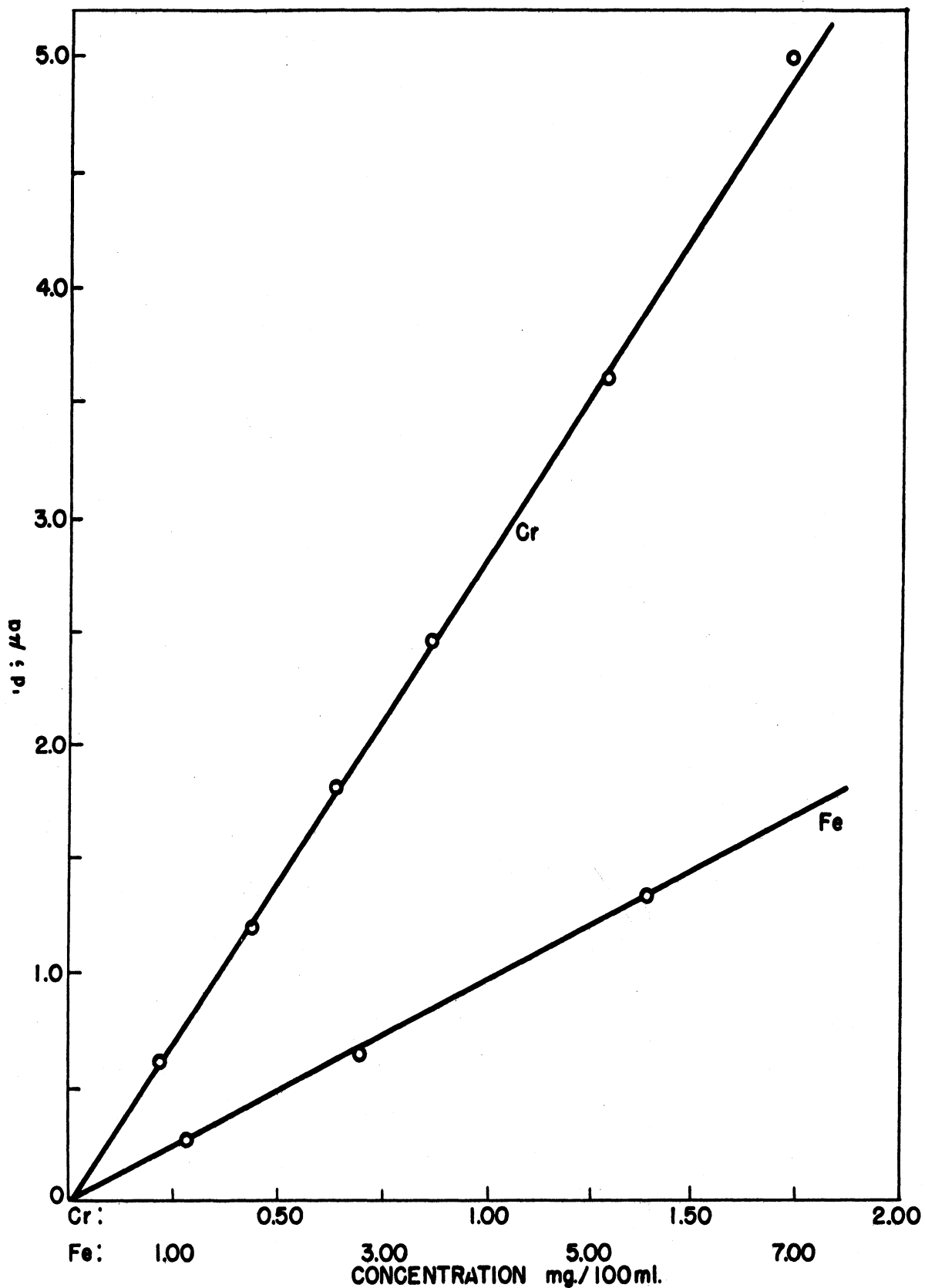


FIG.2. CALIBRATION CURVES FOR POLAROGRAPHIC DETERMINATION OF IRON AND OF CHROMIUM IN 1.0 M KOH AT 25.0°C. IRON PRESENT AS FERRICYANIDE;  $I = 0.49 \mu a$  CHROMIUM PRESENT AS CHROMATE;  $I = 10.7 \mu a$ .

curves which were obtained from standard solutions of iron and chromium. The results obtained thus far for the analysis of one titanium alloy on three separate portions of the sample are tabulated below. Chemical analysis (communicated to us by Dr. Enns) showed 2.14% chromium and 1.06% iron for this sample.

<u>Trial No.</u>	<u>% Cr</u>
1	1.93
2	2.10
3	1.96

The results we obtained for iron were very high, possibly due to the introduction of iron as an impurity in the reagents, but more probably due to a very large residual current caused by other ions in the unknown which were not present in the standard. However, this difficulty will be cleared up in the next few days by examining solutions containing all the elements present in the sample.

#### B. Determination of Vanadium

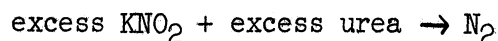
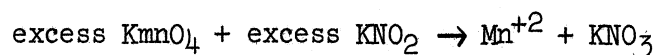
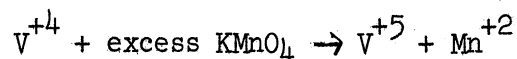
The problem of the polarographic and/or amperometric determination of vanadium in titanium alloys is being attacked. It was found, as noted by Lingane<sup>2</sup>, that  $V^{+5}$  shows a well-defined reduction wave to  $V^{+4}$  in 5% (about 2 M)  $H_2SO_4$ , the wave starting from zero applied potential (i.e., the true half-wave is more positive than the anodic dissolution potential for mercury) with a dropping mercury electrode. The wave height falls off quite rapidly with time, however, due to chemical reduction of the vanadium by metallic mercury. Hence a rotating platinum micro-electrode is being employed in place of the dropping mercury electrode. The lower order of reproducibility of the " $i_d$  vs.  $C$ " relation (between runs) with such an electrode can be offset by employing an amperometric titration technique instead of using direct polarography as a measuring step. The former technique has the advantages, in any case, of being: (1) more versatile (with respect to concentration range embraced); (2) slightly more selective (as regards interferences); and (3) more sensitive for small quantities (current enhanced by rotation).

$V^{+5}$  in 10 mM solution reduces at -0.45 volt (S.C.E.) in 5% sulfuric acid at a platinum electrode. Ferrous ion is a suitable titrant and the  $Fe^{+3}$  to  $Fe^{+2}$  iron potential is about +0.05 volt in 5% acid on platinum. At a fixed potential setting of -0.20 volt (S.C.E.), the amperometric titration of  $V^{+5}$  with  $Fe^{+2}$  should give an increasing current up to the equivalence point, and a levelling off beyond this point. This general behavior is found, but premature (as much as 40% too early) end points and anomalous rounded maxima in the current-volume plots have been observed



in the first trials. It seems reasonably certain that a different potential setting or, if necessary, a change in titrant will overcome this difficulty.

The vanadium technique is (tentatively) being designed around a sulfuric acid medium. This could result from a direct sample dissolution in this medium, but it is contemplated that aliquoting at an appropriate stage in the iron-chromium procedure may give a feasible one-sample technique for V-Cr-Fe. Ideally, this might be accomplished at a point where the vanadium is already in the appropriate +5 oxidation level (subsequent, e.g., to a persulfate oxidation in the Fe-Cr treatment). Otherwise, it seems feasible to make the necessary adjustment via the technique of Long and Kurtz<sup>3</sup> as amplified and studied by Walden, Hammett, and Edmonds<sup>4</sup>. This technique involves the sequence of conversions (equations not balanced):



Any excess of urea is polarographically inactive in the potential range needed to examine vanadium.

#### FUTURE WORK

The cause of the high results for iron will be ascertained. It is then proposed to analyze several known titanium alloys for their iron and chromium content in order to have available further comparative checks on this method. The study of the amperometric method for vanadium will be continued.

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