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PROGRESS REPORT NO. 15

CONTROL INDICES AND ANALYTICAL PROCEDURES

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SUMMARY

The polarographic determination of iron and chromium in a mixed inorganic salt solution has been accomplished by two methods. In the first, chromium is determined as chromate in an alkaline medium. In the second, chromium (as chromate) and iron (in the ferric state) are determined simultaneously in alkaline mannitol solution.

The methods involve a preliminary simple and rapid persulfate oxidation of the chromium to chromate. An accuracy of about 1.5% in the case of chromium and about 4% or better in the case of iron can be achieved.

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SUMMARY OF RESULTS

ANALYTICAL PROCEDURE STUDIES. III. DETERMINATION OF ANALYTICAL PROCEDURES

FOR IRON, CHROMIUM, SULFATE, AND NITRATE IN A MIXED INORGANIC SALT SOLUTION

A. Objective and Implementation

The objective of the present investigation was to develop an accurate and rapid procedure for the determination of chromium and of iron in a mixed inorganic salt solution of composition specified by the sponsoring agency. The composition of this solution is discussed in Progress Report No. 12 and is indicated in a subsequent section of this report.

A review of the existing methods for the determination of chromium and iron suggested several possibilities. Standard titrimetric and gravimetric procedures were found to be too long and involved to be applicable in this investigation.

For a number of reasons photometric methods were considered to be less desirable than electrometric methods. Consequently, attention was focussed on possible polarographic procedures. Of the various polarographic methods which might be used for the purpose, three seemed especially feasible for the purpose of this project.

An alkaline cyanide system for simultaneously determining chromium and estimating iron was recently developed in the University of Michigan Department of Chemistry in connection with an investigation of certain methods of refractory-alloy analysis.

The polarographic determination of chromium as chromate in alkaline solution according to the method of von Stackelberg, Klinger, Koch, and Krath[1]

seemed especially promising, as other metals present in steel apparently do not interfere.

A recently described alkaline mannitol system[2] for the simultaneous determination of chromium and iron also seemed applicable to the solution in question.

One necessary factor common to any satisfactory polarographic method for the determination of chromium is the conversion of chromium to the Cr(VI) state of oxidation. The reduction of the latter species to Cr(III) is a relatively simple and clear-cut process. The reduction of Cr(III) to Cr(II) or Cr(0), on the other hand, is not a satisfactory process due to the complication of the so-called hydrolysis wave. Similarly, in order to get a good iron wave it is necessary to have present either ferrous iron or some suitably complexed ferric iron species. The present system prohibited the use of a ferrous species due to the simultaneous presence of oxidizing agents, e.g., Cr(VI).

B. Determination of Chromium as Chromate in Alkaline Medium

1. Experimental Procedure

Chemicals and Reagents. All chemicals used were of reagent or C.P. grade and were used without further purification.

Nitrogen: Commercial water-pumped grade was purified by passing it through washing bottles filled with alkaline pyrogallol, sulfuric acid, and water, respectively.

Solutions. The solutions used in this investigation were prepared as follows:

Standard chromate and iron solution: 0.1819 gram of reagent-grade ferric oxide was dissolved in about 3.5 ml of 6M sulfuric acid with heating; 1.3 ml of concentrated nitric acid and about 20 ml of water were added; the solution was heated and kept boiling for about 10 minutes. This iron solution (cooled) was then added to 0.1205 gram of reagent-grade potassium dichromate in a volumetric flask and the volume brought up to 500 ml with distilled water.

Mixed inorganic salt solution: This solution was the same as that reported in Progress Report No. 11 and consisted of 22.5116 grams of 347 stainless steel dissolved in 350 ml of 6M sulfuric acid to which were added 3.9 grams of magnesium oxide and 130 ml of 15M nitric acid. A 5-ml portion of this solution was pipetted into a 400-ml beaker and diluted to about 200

ml with distilled water. Then 2.5 ml of concentrated sulfuric acid and a few glass beads were added. The solution was heated to the boiling point and one drop of 0.5M silver nitrate solution and 2 grams of ammonium persulfate were added. The boiling was continued for 10 minutes in order to complete the oxidation and to decompose the excess persulfate. The solution was cooled and the volume brought up to 500 ml with distilled water.

Potassium hydroxide: A 1.6M solution of potassium hydroxide was prepared.

Silver nitrate: A 0.5M solution of silver nitrate was prepared.

1% gelatin solution: 1 gram of gelatin was dissolved in 100 ml of distilled water which had previously been boiled for 10 minutes and then cooled to about 50°C. The solution was cooled to room temperature, a few drops of chloroform were added as a preservative, and the bottle was stoppered with a sterile rubber stopper.

Apparatus. A Sargent Model III manual polarograph was used in conjunction with a dropping-mercury electrode. The drop-time of the latter at open circuit was 3 seconds in distilled water. The cell was a jacketed H-cell with a saturated calomel half-cell connected to the sample-solution cell by means of a saturated potassium chloride - agar bridge[3]. Constant temperature was maintained at 25.0 $\pm$ 0.1°C by means of thermostatically controlled water pumped through the cell.

Analytical Procedure. A 5.00-ml aliquot of the sample solution was pipetted into a 100-ml volumetric flask and 50 ml of 1.6M potassium hydroxide solution was added, along with 0.5 ml of 1% gelatin solution. The volume was then brought up to 100 ml with distilled water and the solution mixed thoroughly. A portion of the nearly clear supernatant liquid of this solution was transferred to the polarographic H-cell and deoxygenated with nitrogen for 10 minutes. The current-potential curve was then obtained over the range of -0.5 v to -1.5 v vs S.C.E. A nitrogen atmosphere was maintained over the surface of the solution during electrolysis.

2. Data Obtained and Interpretation

Determination of Experimental Conditions. It was found that addition of 0.5 ml of 1% gelatin gives a better defined curve than that obtained in the absence of gelatin. Careful temperature control was also found to contribute to better reproducibility of the diffusion currents.

Results Obtained. A typical polarogram obtained is shown in Fig. 1. Two solutions of known potassium dichromate content were analyzed by

FIG. I
POLAROGRAM OF CHROMIUM (VI)
IN ALKALINE SOLUTION
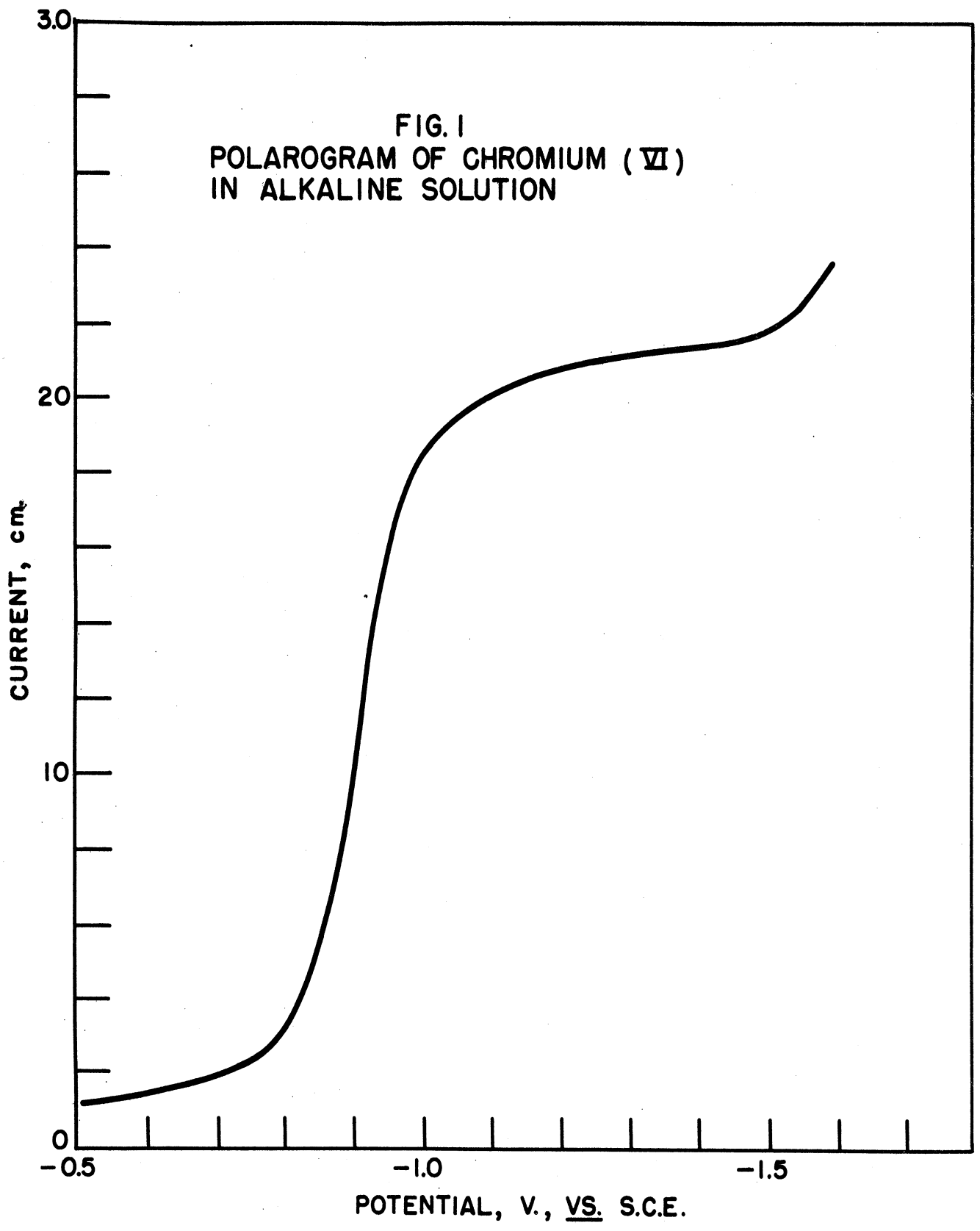
the procedure given; these were prepared by different dilutions of the standard chromium and iron solution. The results, shown in Table I, are quite satisfactory. The ratio of the individual average current/concentration ratios is 1.03, which differs from unity by about the magnitude of error expected in polarographic measurement.

TABLE I

POLAROGRAPHIC DETERMINATION OF CHROMIUM
IN $K_2Cr_2O_7$ AND IN MIXED INORGANIC SALT SOLUTIONS

Sample Solution	Cr Concentration, mg/100 ml	Measured Currents, cm	Average Current, cm	Standard Deviation
$K_2Cr_2O_7$	0.426	17.5 17.7 17.9	17.7	0.2
$K_2Cr_2O_7$	0.341	14.2 13.7 14.1 13.7	13.8	0.3
Mixed Inorganic Salt	0.419	17.0 17.1 17.2 17.1 16.9	17.1	0.1

The sample of mixed inorganic salt solution was similarly analyzed polarographically (Table I). Calculation of the concentration from the data in Table I for the two known chromium solutions gave values of 0.411 and 0.421 mg Cr/100 ml. An independent check on the chromate concentration in the oxidized solution of the mixed inorganic salt solution sample was obtained by adding an excess of a standard solution of ferrous ethylenediamine sulfate and then back-titrating with a standard potassium dichromate solution; a value of 0.419 mg Cr/100 ml was obtained. This value, compared to those calculated from the two known chromium solutions, corresponds to an average error of 1.2%. In view of the expected 2 or 3% accuracy for any polarographic method, this agreement is quite satisfactory.

As seen from Table I, individual samples in each series give excellent agreement, except in the case of the more dilute standard chromium

solution, although the deviation (2.2%) is well within the accuracy limits specified by the outline for the Analytical Procedure Studies.

The average half-wave potential of the chromate ion reduction wave observed was -0.88 v vs the S.C.E. This compares quite well with -0.85 v vs S.C.E. as reported by Kolthoff and Lingane[1]. The slight variation may be due in part to the IR drop originating in the resistance of the cell.

C. Determination of Iron and Chromium in Alkaline Mannitol Medium

1. Experimental Procedure

Chemicals and Reagents. The following chemicals and reagents were used:

d-Mannitol: Pfanstiehl C.P. grade (m.p. 166°C)
Potassium hydroxide solution: 10M.

Solutions. The solutions used in this investigation were prepared as follows:

Mixed inorganic salt solution: This was the same persulfate-oxidized solution as that used in the determination of chromium as chromate in alkaline medium (previous section).

Standard chromate and iron solution: This was the solution used in the determination of chromium as chromate in alkaline medium (previous section).

Apparatus. Both a Sargent Model III manual polarograph and a Leeds and Northrup Model E recording polarograph were used in conjunction with a dropping-mercury electrode. The drop-time of the latter (on open circuit) was 7.5 seconds in distilled water at 25°C. The polarographic cell and temperature control were the same as those previously described.

Analytical Procedure. A solution of 30 ml of 10M KOH was added to 3.6 grams of mannitol in a 100-ml volumetric flask; 5.00 ml of chromate and iron sample solution was then pipetted into the flask; the volume was brought up to 100 ml with water. A portion of the solution was transferred to the polarographic cell, and after 10 minutes of nitrogen bubbling the polarogram was taken over an applied potential range of -0.4 v to -1.6 v vs S.C.E. A nitrogen atmosphere was maintained over the solution during electrolysis.

2. Data Obtained and Interpretation

Determination of Experimental Conditions. It was noticed that unless the capillary was cleaned with nitric acid and distilled water following each run, the drop-time of the electrode varied. This was probably due to the effect on the glass of the highly concentrated alkaline solution. Even frequent cleaning did not entirely eliminate this variability, but the variation was so small that it would not be appreciable in the value of the diffusion current.

It is extremely important that a long drop-time be used; otherwise, poor wave shapes are obtained with alkaline solutions due to "an electrical instability effect"[2]. The optimum drop-time is from 6 to 7 seconds.

The polarographic test solutions should be run soon after they are prepared; it was found that a delay of several hours.causes the chromium and iron diffusion current values to decrease.

Results Obtained. Figure 2 shows a typical polarogram obtained in alkaline mannitol solution.

Several dilutions of the standard chromate and iron solution were analyzed polarographically in replicate to yield the results tabulated in Table II. When plotted, these data give two straight lines.
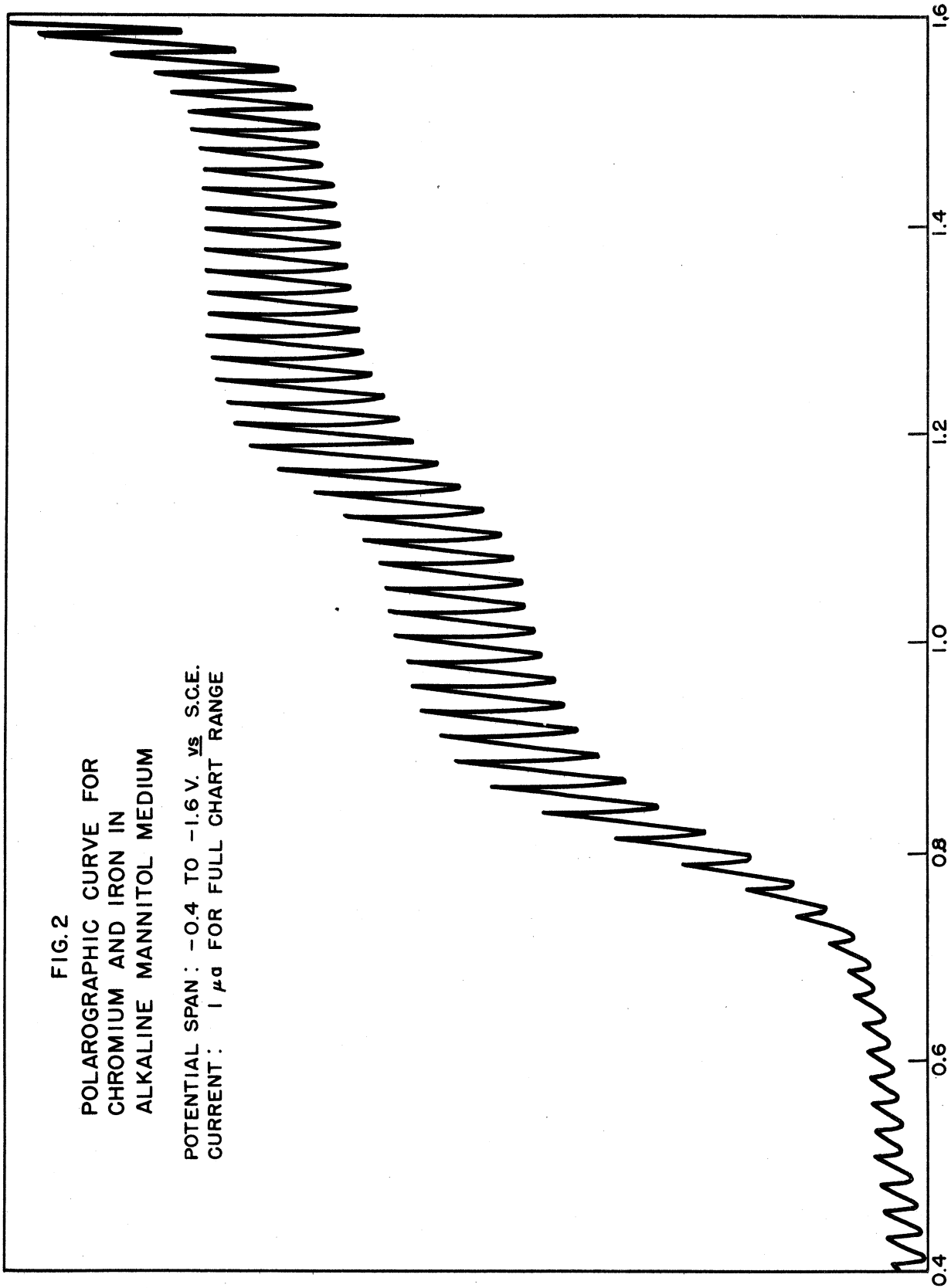
TABLE II

DIFFUSION CURRENTS OBTAINED FOR IRON AND CHROMIUM IN STANDARD SOLUTIONS

Iron Wave		Chromium Wave	
Concentration, mg/100 ml	i_d, 10^{-2} μa	Concentration, mg/100 ml	i_d, 10^{-2} μa
0.761	15.5	0.256	40.0
0.761	14.8	0.256	39.0
1.014	21.4	0.3409	54.5
1.014	21.4	0.3409	54.6
1.268	27.8	0.426	66.8
1.268	24.8	0.426	65.8
1.268	25.8	0.426	67.4
1.522	31.2	0.511	80.0
1.522	30.0	0.511	78.0

FIG. 2

POLAROGRAPHIC CURVE FOR
CHROMIUM AND IRON IN
ALKALINE MANNITOL MEDIUM

POTENTIAL SPAN: −0.4 TO −1.6 V. vs S.C.E.
CURRENT: 1 μa FOR FULL CHART RANGE

The oxidized sample of the mixed inorganic salt solution was analyzed in quadruplicate; the measured diffusion currents for iron and chromium are given in Table III.
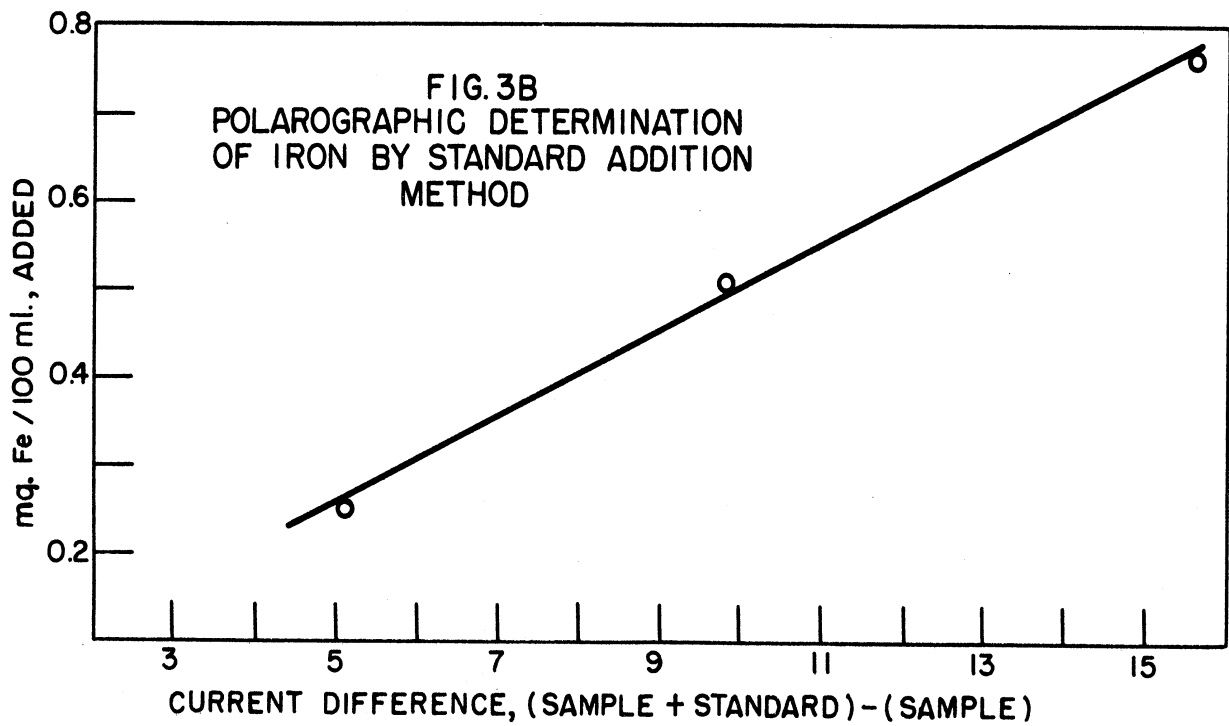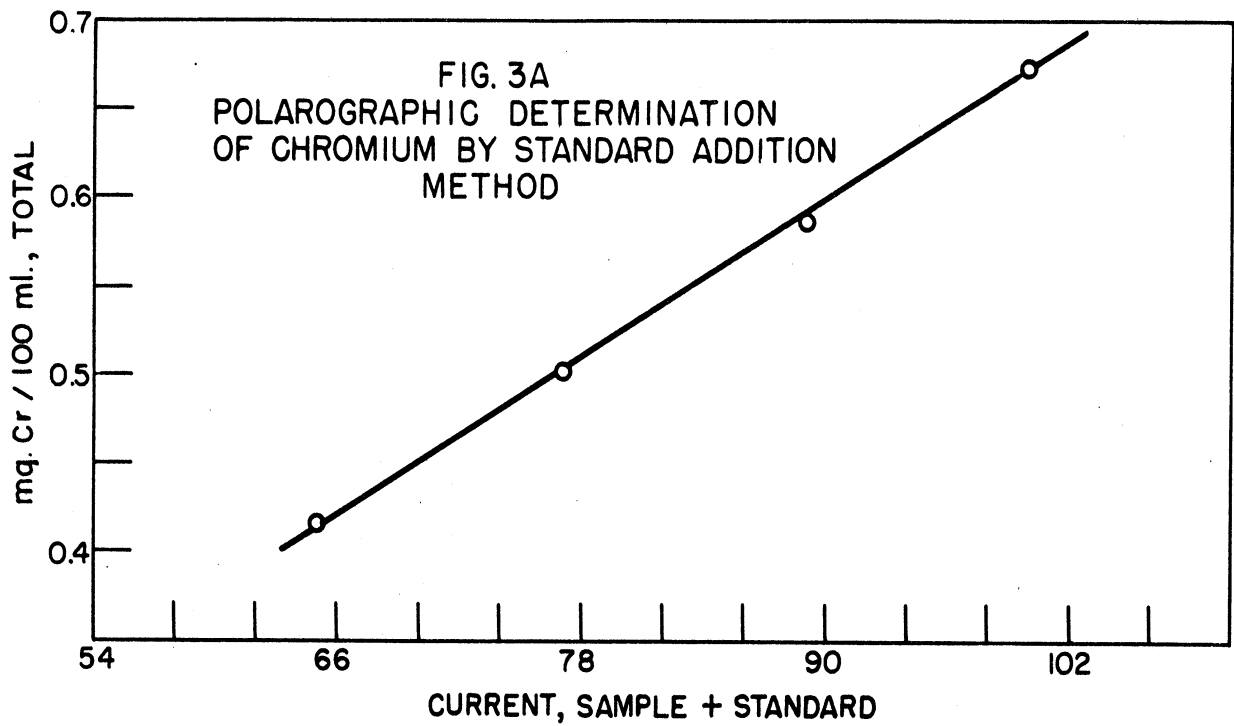
TABLE III

DIFFUSION CURRENTS OBTAINED FOR IRON AND CHROMIUM
IN AN OXIDIZED MIXED INORGANIC SALT SOLUTION

Element	i_d, 10^{-2} μa	Average i_d, 10^{-2} μa
Fe	9.9 9.5 9.0 9.8	9.5
Cr	65.0 65.1 64.7 64.7	64.9

Since it was estimated that the mixed inorganic salt solution when it was prepared for polarographing would contain about 1.3 mg of iron per 100 ml, the value of the diffusion current predicted from Table II is about 26×10^{-2} μa. Actually, however, a value of 9.5×10^{-2} μa, corresponding to 0.478 mg iron per 100 ml, was obtained. It would appear that the magnitude of the diffusion current of the ferric-mannitol complex is dependent on the presence and perhaps the concentration of the various other ions in the solution of 347 stainless steel and other components. This is not surprising since, as stated in Reference 2, variation in the absolute concentrations of iron, chromium, or both will also cause mutual interference of the two waves. Therefore, the direct standard-series comparison method cannot be used for analytical purposes in the inorganic mixed salt solution.

It was considered possible that the effects of interference between the iron and chromium waves would be minimized if the ratio of the iron and chromium concentrations were kept fairly constant, even though the absolute concentrations increased. Consequently, the method of standard addition, slightly modified for convenience in calculation, was tried. This method consisted of adding to 5.00-ml portions of the mixed inorganic salt solution (persulfate-oxidized) 1.00, 2.00, or 3.00 ml of standard chromate and iron solution. Then 30 ml of 10M KOH solution and 3.6 grams of mannitol were added and the volume brought up to 100 ml with distilled water. Then the

FIG. 3A
POLAROGRAPHIC DETERMINATION
OF CHROMIUM BY STANDARD ADDITION
METHOD

CURRENT, SAMPLE + STANDARD

FIG. 3B
POLAROGRAPHIC DETERMINATION
OF IRON BY STANDARD ADDITION
METHOD

CURRENT DIFFERENCE, (SAMPLE + STANDARD) - (SAMPLE)

polarogram is taken as previously described. The data thus obtained are
shown in Table IV. and Fig. 3.

TABLE IV

WAVE HEIGHTS OF CHROMIUM AND IRON IN ALKALINE MANNITOL SOLUTION:

ADDITION OF STANDARD CHROMIUM AND IRON SOLUTION
TO A SAMPLE OF MIXED INORGANIC SALT SOLUTION

Chromium Wave		Iron Wave	
Amount Added, mg	Wave Height, 10^{-2} μa	Amount Added, mg	Wave Height, 10^{-2} μa
0.000*	65.0 65.1 64.7 64.7	0.000*	9.8 9.5 9.0 9.8
0.085	76.9 77.3	0.254	13.9 15.2
0.170	89.0 89.0	0.508	19.4 19.2
0.256	105.8 102.2	0.767	26.0 24.8

*Original sample solution.

Interpretation of Results. As seen in Table IV and Fig. 3, the
method of standard addition gives a straight-line relationship. It would
appear, therefore, that the magnitudes of the diffusion currents obtained
for iron and chromium in this manner are not dependent on the relative con-
centrations of the other ions present in the mixed inorganic salt solution,
or at least the variations are too small to be significant over the short
concentration range in question. Any slight variation in the ratio of
chromium and iron concentrations introduced by the standard added does not
affect the wave heights significantly. The alkaline-mannitol procedure is,
therefore, suitable for analytical measurement.

An error of about 1% is involved in the alkaline-mannitol proce-
dure for chromium. As the amount of iron in the mixed inorganic salt solu-
tion was not accurately known, only a relative error may be stated in the

case of iron; this relative error was about 4% and was estimated by noting the difference between the observed and known values of concentrations of standard iron solution added to 5 ml of mixed inorganic salt solution. The absolute error is undoubtedly smaller, but unfortunately lack of time prevented an independent check.

It was observed that the residual-current portions of the curves were often very erratic in shape, although their slopes remained constant. These slopes were considerably steeper than those noted by Perkins and Reynolds[2].

In determining the heights of the polarographic waves, the method of extrapolation of the residual-current curve was used. Although this method yielded the required accuracy, it may be that another method of measurement would give higher precision.

The average half-wave potentials obtained for the chromium and iron waves were -0.80 v vs S.C.E. and -1.15 v vs S.C.E., respectively. Reference 2 does not specify exactly the half-wave potentials of iron and chromium used in the alkaline-mannitol procedure. In order to minimize interference of the two waves with each other, it is necessary to have the polarographic-cell test solution at the low chromium and iron concentrations used in this report.

D. Determination of Iron and Chromium in Alkaline Cyanide Medium

A series of experiments using the alkaline cyanide system as polarographic background showed the results obtained to be extremely dependent on reproducible timing in each run. Since more work would have been necessary to determine the optimum operating conditions, and since the other two background systems seemed more promising, no further work was done. A third wave, due to nickel, was obtained in the alkaline cyanide solution.

E. Literature Cited

1. Kolthoff, I.M., and Lingane, J.J., Polarography, vol. II, Interscience Publishers, New York, 1952, p. 612.

2. Perkins, M., and Reynolds, G.F., Analyst, 78, 480-7 (1953).

3. Komyathy, J.C., Malloy, F., and Elving, P.J., Anal. Chem., 24, 431 (1952).