POLAROGRAPHIC DETERMINATION OF MANGANESE OR COPPER IN CARBON STEELS

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Introduction

Recently, a new polarographic method for the determination of manganese and iron in steel, cast iron, ores, and synthetic mixtures has been reported by Issa, Issa, and Hewaidy (1958). This method involves the measurement of the polarographic reduction waves for Mn(III) to Mn(II) and Fe(III) to Fe(II), following suitable preliminary oxidation and complexation treatment. In an attempt to employ this method in the analysis of certain National Bureau of Standards carbon steel samples, the present authors found that the method yields erroneous results when the steel samples contain copper. It was further noted that the observed error in the measured manganese content depended upon the amount of copper present in the steel. This error appears because the polarographic reduction of Cu(II) occurs at approximately the same potential as that of Mn(III), resulting in an increase in the measured height of the Mn(III) wave due to coalescence of the latter with the Cu(II) wave. Consequently, high results for manganese are always obtained in the presence of amounts of copper exceeding about 0.01%.

The error due to copper may be eliminated by preliminary treatment of the sample, in acidic solution, with metallic zinc (Riha, 1952). However, it appeared possible to employ the copper interference to advantage in adapting the method to a two-fold purpose, i.e., the accurate determination of either manganese or copper.

Apparatus and Reagents

The Leeds and Northrup Electro-Chemograph, Type E, was employed, using a Fisher Electrode Stand Assembly. All potential measurements were made *vs.* the saturated calomel electrode. The capillary used as the dropping mercury electrode was made of Pyrex brand glass and had an m value of 2.312 mg./sec., measured at open circuit in distilled water. All polarographic measurements were made in an air-conditioned room where the temperature was maintained at 25 $\pm$ 1°C.

The iron used was Mallinckrodt Analytical Reagent Grade electrolytic wire; standard iron test solutions were prepared as subsequently described. A stock solution of manganous nitrate (Baker Analyzed) was prepared by dissolving the requisite weight of the reagent in water and diluting to 100 ml. in a volumetric flask; the final solution contained 1.000 mg. of manganese per ml. Various predetermined volumes of the manganous nitrate solution were added to standard iron test solutions in order that each test solution might contain the desired concentrations of manganese and iron. The Triethanolamine used as a complexing reagent was Eastman Kodak No. 1599. All other reagents were ana-

lytical reagent grade or equivalent.

Preliminary Polarographic Procedure

Standard iron test solutions were prepared by dissolving exactly 1.000 gram samples of electrolytic iron in 10 ml. of 50% nitric acid and adding 5 ml. of water. The solutions were boiled to expel oxides of nitrogen. The required volume of manganous nitrate stock solution was added to each test solution and the latter then brought up to volume and properly mixed in a 100-ml. volumetric flask. A 10-ml. aliquot portion (pipet) was removed and added to 8 ml. of 50% triethanolamine contained in a 25-ml. volumetric flask; 2.5 ml. of 5 *M* sodium hydroxide were added, followed by 2 drops of 3% hydrogen peroxide. Approximately 0.2 gram (a slight excess) of solid sodium sulfite was then added, the solution properly mixed and diluted to volume. Twenty ml. of the sample solution were transferred to the polarographic cell, purged with nitrogen for 10 minutes in order to expel any residual oxygen and then polarographed.

Diffusion Current Measurement

The method usually used for measurement of the total polarographic diffusion current is the single point method (Willard, Merritt, and Dean, 1958, pp. 544-5). This method was employed in the measurement of the total diffusion currents for the polarograms obtained as previously described, yielding results which were consistently low. This error was attributed to two geometrical factors: (1) the fact that a large Fe(III-II) wave immediately followed the Mn(III-II) wave; and (2) coalescence of a small Cu(II-I) wave, resulting from the presence of small amounts of copper in the steel samples, with the Mn(III-II) wave. The latter occurred because the copper wave in this system differs from that of the manganese wave by less than 0.1 volt.

Two methods exist by which correction may be made for the geometrical effect of one polarographic wave on another; these are the mid-point method (Elving and Van Atta, 1954) and the two-point method. The mid-point method, which requires that all reduction waves be recorded, was considered to be impractical because of the large concentration of iron in the polarographic sample. In the two-point method, two suitably chosen fixed potentials are selected, in this case -0.33 and -0.68 volt *vs.* S. C. E. for the residual and limiting current potentials, respectively, and the diffusion current is determined as the difference between the currents measured at the two points. A typical recorded polarogram for a steel is shown in Figure 1.

Copper Interference in the Determination of Manganese

In order to utilize the method of Issa, Issa, and Hewaidy (1958) for the determination of manganese in carbon steels, a manganese calibration curve was required. This was obtained by preparing and polarographing synthetic test solutions, as described in the preliminary polaro-

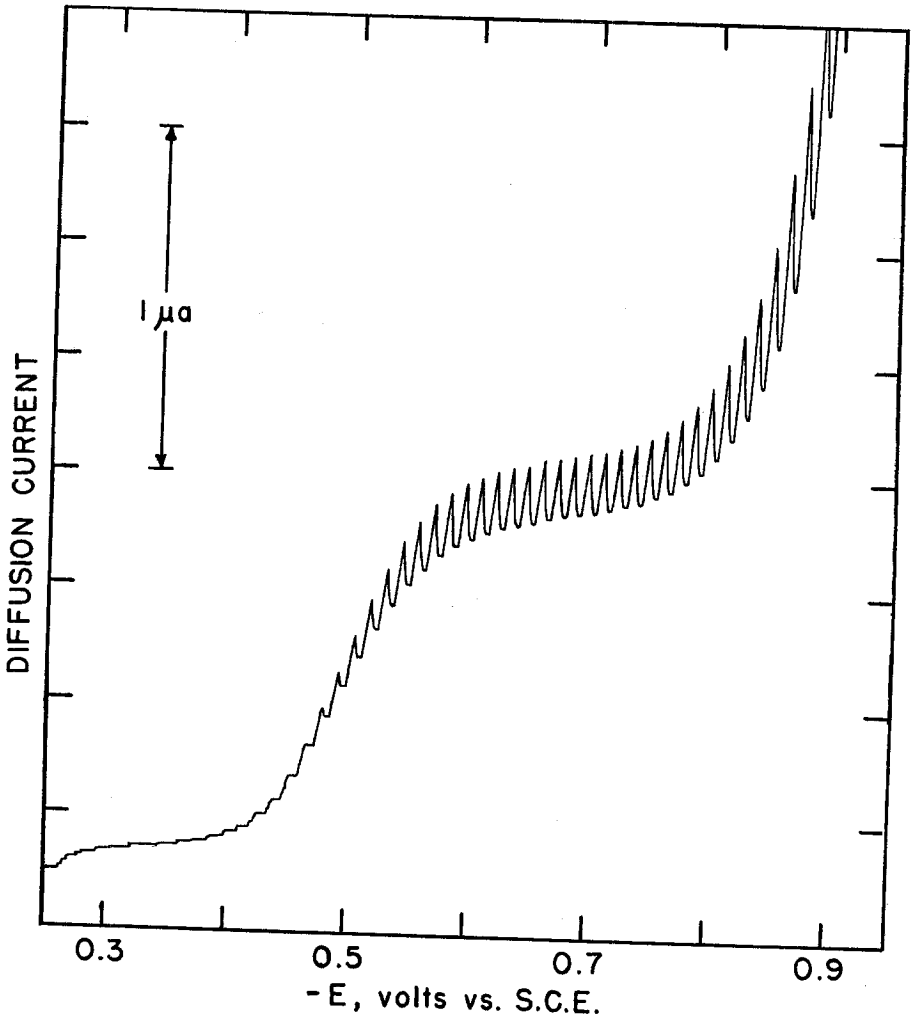

Fig. 1.—A typical recorded polarogram for N.B.S. standard steel No. 8h.

graphic procedure above. The final concentration of manganese, as determined by the quantity of manganous nitrate added to each iron test solution, ranged from 0.0% to approximately 1.0%. By plotting the measured diffusion current *vs.* the concentration, a linear calibration curve was obtained. This curve did not pass through the origin since there was a small manganese-copper impurity in the electrolytic iron stock solutions. Since this manganese-copper concentration was peculiar only to the synthetic steels and was shown to be of constant magnitude, a corrected manganese calibration curve was constructed

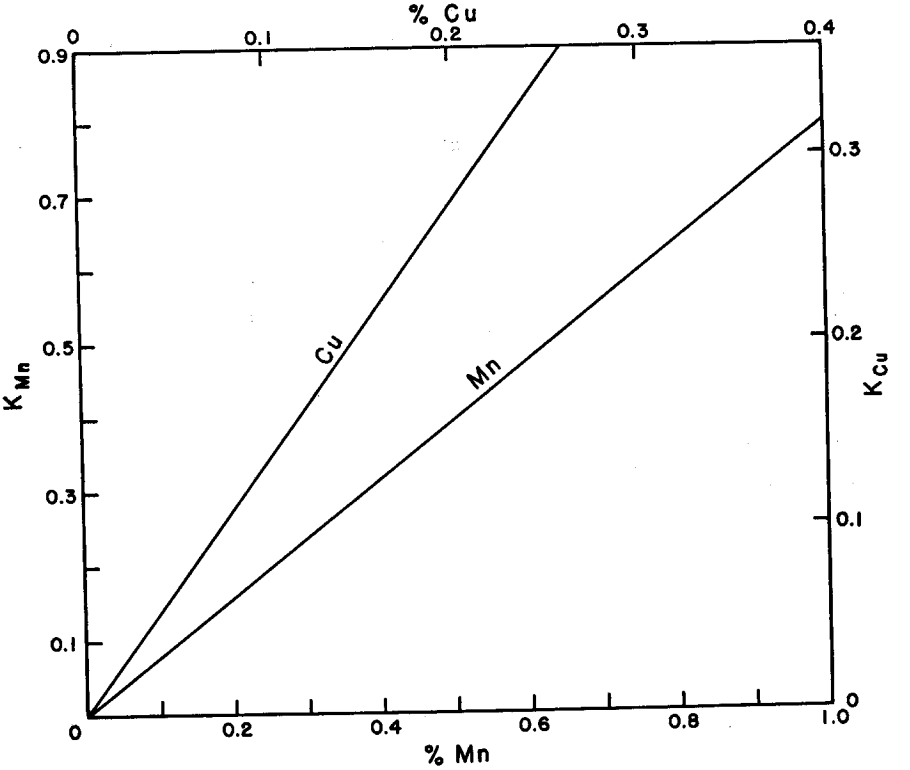

Fig. 2.—Calibration curves for the polarographic determination of manganese or copper in carbon steels. *A*. Determine $K_{(Mn + Cu)} = \frac{{}^{i}d_{(Mn + Cu)}}{{}_{m}2/3{}_{t}1/6}$ experimentally. *B*. From known %Mn or %Cu, read K_{Mn} or K_{Cu}. *C*. $K_{Mn} = K_{(Mn + Cu)} - K_{Cu}$; $K_{Cu} = K_{(Mn + Cu)} - K_{Mn}$. *D*. Determine %Mn or %Cu from K_{Mn} or K_{Cu}.

and used in conjunction with the analysis of carbon steel samples. In order that the curve might be used with various capillaries, $K = {}^{i}d_{Mn}/{}_{m}2/3{}_{t}1/6$ was plotted *vs.* % Mn, rather than ${}^{i}d_{Mn}$ (Fig. 2).

Table I shows the results obtained in the determination of manganese in National Bureau of Standards carbon steel samples, using the method of Issa, Issa, and Hewaidy (1958) and the corrected calibration curve. In each case the percentage of manganese obtained was high and the degree of error was related to the copper content present; other components in the steel appear to have no detectable effect on the measured manganese content.

TABLE I.—Polarographic Analysis of National Bureau of Standards Steels. (Current measured at -0.33 and -0.68 volt.)

NBS Steel	NBS Cu	NBS Mn	Mn Measured*		Mn Measured**	
			Found	Relative Error	Found	Relative Error
No.	%	%	%	%	%	%
12f	0.121	0.838	1.045	+24.7	0.835	—0.36
152	0.127	0.782	0.998	+27.8	0.781	—0.13
20f	0.238	0.734	1.140	+35.6	0.726	—1.09
10f	0.032	0.642	0.708	+10.3	0.652	+1.56
19f	0.151	0.497	0.763	+53.5	0.499	+0.40
8h	0.054	0.454	0.556	+22.5	0.461	+1.54
16d	0.052	0.439	0.535	+21.9	0.444	+1.14
14d	0.084	0.399	0.550	+37.8	0.401	+0.50
15f	0.085	0.390	0.530	+35.9	0.384	—1.54
170	0.102	0.226	0.403	+78.3	0.225	—0.44

* Manganese content by method of Issa, Issa, and Hewaidy (1958).
** Manganese content by modified procedure.

The correction for copper concentration was accomplished by polarographing several National Bureau of Standards carbon steel samples in which both the manganese and copper contents were known. The total diffusion current, $i_{d\,(Mn + Cu)}$ was measured as previously described; the $i_{d\,Mn}$ was subtracted, as determined by the analyzed content of manganese and the manganese calibration curve. The resulting diffusion current was the contribution due to the copper present in the steel. In the analysis of several steel samples ranging in copper content from 0.032 to 0.238% (NBS standard sample numbers: 10f, 20f, 14d, and 152), a linear calibration plot of the concentration of copper *vs.* measured diffusion current $(i_{d\,Cu}/m^{2/3}t^{1/6})$ was obtained (Fig. 2). By applying a correction to the total diffusion current for the amount of copper present, as determined from the analyzed copper content and the copper calibration, the data for the manganese content yielded results well within permissible instrumental error (Table I).

By reversing the technique described, the copper content of carbon steels may be determined. Such a procedure involves the measurement of the total diffusion current for the Mn(III) and Cu(II) waves as in the manganese determination. The K_{Mn} is evaluated from the manganese calibration curve and the known or previously determined manganese content. The total meas-

TABLE II.—Analysis for Copper.

NBS Steel	NBS[1] Mn	NBS[2] Cu	Cal[3] Curve	Absolute Error	Relative Error
No.	%	%	%	%	%
16d	0.439	0.052	0.053	+0.001	+1.92
8h	0.454	0.054	0.055	+0.001	+1.85
15f	0.390	0.085	0.083	—0.002	—2.35
170	0.226	0.102	0.102	0.000	0.00
12f	0.836	0.121	0.122	+0.001	+0.82
19f	0.497	0.151	0.152	+0.001	+0.66
20f	0.734	0.238	0.236	—0.002	—0.84

1 Determined colorimetrically.
2 Reported average of various methods.
3 Average of three individual analyses.

ured value, $K_{(Mn+Cu)}$, is then corrected for the current contribution due to the manganese present, yielding the K_{Cu} value. Using the copper calibration curve, the copper content of the steel was determined. The results for the determination of copper by use of the modified method are shown in Table II. Results obtained in this manner compare favorably with other methods for the determination of copper (*i.e.* by the electrolytic, diethyldithiocarbamate photometric and copper ammonia complex photometric procedures).

SUMMARY

The results of this investigation show that the method of Issa, Issa, and Hewaidy for the determination of manganese in carbon steels gives erroneous results when the copper content is greater than 0.01%. A modified method yielding satisfactory results is presented whereby either copper or manganese may be determined provided that one or the other concentration is known.

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Manuscript received November 21, 1960.