

# Successive Potentiometric Titration of Copper and Iron in Metallurgical Products<sup>1</sup>

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SINCE the reactions of copper and iron in solution are very similar, the accurate determination of either of these elements by means of the accepted gravimetric or volumetric methods presupposes a separation of one from the other, and such separation is, as a rule, time consuming. Potentiometric methods have in recent years been applied individually to copper<sup>2</sup> and iron,<sup>3</sup> but the writers have found only the work of Tomicek<sup>4</sup> and Kolt-hoff<sup>5</sup> on the successive electrometric titration of these two elements, which will be discussed later in this paper.

Since the potentiometric method for iron alone is sufficiently well established, it was considered best to confine the attention in this paper to the study of copper alone and of copper-iron mixtures. As above stated, the properties of copper and iron in solution present a number of similarities: they both form insoluble hydroxides, sulfides, ferrocyanides, and complex chloro ions; they also occur in two stages of oxidation. Preliminary experiments showed that the precipitation method would be out of the question, but that a suitable oxidation or reduction method might be feasible. Table I<sup>6</sup> was used as a basis of choosing conditions and reagents.

Table I—Molal Reduction Potentials of Certain Ions and Metals

		Volt
Cr <sup>++</sup> →	Cr <sup>+++</sup>	+0.43
Ti <sup>++</sup> →	Ti <sup>+++</sup>	+0.00
H <sub>2</sub> →	H <sup>+</sup>	0.00
Sn <sup>++</sup> →	Sn <sup>+++</sup>	-0.14
Cu <sup>+</sup> →	Cu <sup>++</sup>	-0.17
Hg <sub>2</sub> Cl <sub>2</sub> →	Hg <sup>++</sup>	-0.24
Cu <sup>0</sup> →	Cu <sup>+</sup>	-0.34
Fe <sup>++</sup> →	Fe <sup>+++</sup>	-0.75
Cr <sup>+++</sup> →	HCrO <sub>4</sub> <sup>-</sup>	-1.3

On the basis of these reduction potentials, a study of the problem was planned from the following points of view:

1—Complete reduction followed by titration with standard dichromate

- (a) SnCl<sub>2</sub>-HgCl<sub>2</sub> combination as in Penny's method
- (b) Excess SnCl<sub>2</sub> added and titration with dichromate
- (c) Excess TiCl<sub>3</sub> added and titration with dichromate
- (d) Excess CrCl<sub>2</sub> added and titration with dichromate

<sup>1</sup> Presented under the title "The Successive Electrometric Titration of Copper and Iron in Metallurgical Products" before the joint session of the Divisions of Industrial and Engineering Chemistry and Cellulose Chemistry and the Section of Paint and Varnish Chemistry at the 70th Meeting of the American Chemical Society, Los Angeles, Calif., August 3 to 8, 1925.

<sup>2</sup> Zintl and Wattenberg, *Ber.*, **55**, 3366 (1922); Willard and Fenwick, *J. Am. Chem. Soc.*, **41**, 1337 (1919).

<sup>3</sup> Hildebrand, *Ibid.*, **35**, 869 (1913); Hostetter and Roberts, *Ibid.*, **41**, 1337 (1919).

<sup>4</sup> *Rec. trav. chim.*, **43**, 800, 812 (1924).

<sup>5</sup> *Ibid.*, **43**, 820 (1924).

<sup>6</sup> Treadwell-Hall, "Qualitative Analysis," Vol. I, 1921, p. 44; Gerke, *Chem. Rev.*, **1**, 377 (1925).

In order to eliminate the necessity of separating copper from iron in analytical procedure, as is now generally required by all the accepted gravimetric and volumetric methods owing to the similarity of their properties in the dissolved state, the successive potentiometric titration of these elements has been studied. Both direct and indirect methods of titration involving reduction with stannous or titanous chloride have been found unsatisfactory. When chromous chloride is used as the reducing agent, either by direct titration or by residual titration with dichromate, the determination of copper and iron, both singly and in their mixtures, is both accurate and rapid. When applied to certain copper smelter products, the methods involving chromous chloride can be recommended in point of accuracy, simplicity, and economy of time, expense, and effort. The reactions involved are deduced on the basis of standard molal reduction potentials of the ions in question, and sources of error in each case are discussed.

2—Direct electrometric titration with standard reducing agents

- (a) Stannous chloride
- (b) Titanous chloride
- (c) Chromous chloride

## Preparation of Materials

The copper chloride solution was prepared from C. P. copper wire by dissolving in nitric acid, removing the excess nitric acid completely by evaporating to dryness with an excess of concentrated hydrochloric acid, and heating the dry salt on the hot plate until brown fumes were no longer given off. The hydrochloric acid solution of this salt was standardized both volumetrically and electrolytically. The iron solution was made up from ferric chloride, which was tested and found free from reducible impurities. It was standardized both volumetrically by Penny's method and potentiometrically. Samples of these solutions were weighed out from a weight pipet. The potentiometric titration unit was of the Hostetter and Roberts type, in combination with platinum and calomel electrodes. The solution was stirred vigorously by means of a mechanical stirrer. To exclude atmospheric oxygen, a layer of kerosene about an inch deep was placed over the solution, through which the stirrer, buret tip, and electrodes extended. The use of kerosene for excluding air was far more certain than the usual method of titrating in the presence of nitrogen, hydrogen, or carbon dioxide, and the solubility of the air in the kerosene appeared to be negligible.

Note—P. S. Danner states that unsaturated hydrocarbons in kerosene greatly increase the solubility of oxygen, and suggests that they be first removed by successive treatment with several changes of concentrated sulfuric acid.

The stannous chloride solution was prepared from crystalline salt and the titanous chloride from a 15 per cent solution. Chromous chloride was prepared according to Evans,<sup>7</sup> by boiling potassium dichromate in hydrochloric acid solution with a considerable excess of arsenic- and iron-free zinc until reduction to the light blue solution was complete. This solution was immediately covered with a layer of kerosene and transferred to the reagent bottle by pipetting under kerosene. It was standardized very easily against standard dichromate solution using the potentiometric indicator (Figure 1). Although extremely sensitive to oxygen, as Table II will show, the solution was found to maintain a fairly constant normality.

Table II—Stability of Chromous Chloride Solution

Days	0	1	3	4	5.5	6.5	8
Normality	0.0927	0.0921	0.0923	0.0919	0.0919	0.0918	0.0916

<sup>7</sup> "Metals and Metallic Compounds," Vol. II, p. 304.

In standardizing the dichromate solution, concordant results were obtained only by employing as a standard the Sibley Iron Ore No. 27 of the United States Bureau of Standards.

### Titration with Potassium Dichromate after Reduction with Various Reducing Agents

#### Stannous-Mercuric Chloride

The procedure of Penny's method for iron was first tried out on copper alone. From the reduction potentials it was regarded as a foregone conclusion (a) that copper would hardly be reduced completely by stannous chloride, and (b) that cuprous ion would react with mercuric ion present. Both of these factors would lead to low results for copper. Experiments showed, in fact, that while the titration curves were

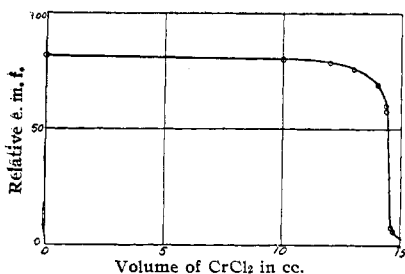


Figure 1—Titration of Potassium Dichromate by Chromous Chloride in Standardizing Chromous Chloride

satisfactory the results were uniformly low in amounts varying from 0.4 to 12.0 per cent. Conditions of concentration, acidity, volume of stannous chloride used for reduction, and amount of mercuric chloride solution used for removal of excess stannous were varied over wide limits. As to completeness of the reduction with stannous chloride, the discharge of the intense olive green solution of cupric chloride acidified with hydrochloric acid to a perfectly water white solution is believed to be evidence of complete reduction to chlorocuprous acid,  $H_2Cu_2Cl_4$ . The low results must therefore be attributed to reaction of the chlorocuprous acid with the mercuric chloride. This was proved by allowing the solution, after reduction, to stand different periods of time in the presence of excess mercuric chloride. The results obtained are shown in Table III.

Table III—Effect of Mercuric Chloride on Chlorocuprous Acid

Cu taken Gram	Time of standing Minutes	Cu found Gram	Per cent error
0.1009	55	0.0846	-16.2
0.1018	90	0.0800	-21.3
0.0977	115	0.0709	-27.4

This observation precluded the use of the stannous-mercuric combination, except for the case of very low acidity where the cuprous chloride precipitates out:  $H_2Cu_2Cl_4 = 2CuCl + 2HCl$ . Although under this condition the rate of reaction with mercuric chloride is greatly decreased, the titration of the solid cuprous chloride is rendered impracticable, because the reaction is too slow.

To overcome this difficulty and yet be able to use stannous chloride for reduction, it was considered desirable to eliminate the mercuric chloride entirely and to titrate selectively the excess of stannous ion present. This, however, was unsuccessful, because the oxidation potentials of cuprous and stannous ion are practically equal, so that only one inflection point was obtained in the titration curve corresponding to the simultaneous oxidation of both.

#### Titanous Chloride

The method of Zintl and Wattenberg,<sup>2</sup> who first reduce with excess titanous chloride, followed by titration selectively with potassium dichromate, was also studied in this connection with a view of applying it to the determination of both iron and copper. When applied to iron it yielded absolutely the

same results as are obtained by other standard methods. In the case of copper, however, for which they claim accuracy and reliability over widely varying conditions, the writers not only failed to confirm their work, but found considerable positive or negative variations. Determinations made under identical conditions, for instance, did not agree, as shown in Table IV.

Table IV—Titration of Copper with Dichromate after Reduction with Titanous Chloride

Volume of soln. Cc.	Per cent HCl	Temperature ° C.	Cu taken Gram	Cu found Gram	Per cent error
70	11	30	0.1330	0.1320	-0.7
70	11	30	0.1319	0.1317	-0.2
25	30	30	0.0772	0.0790	+2.3
25	30	80	0.0766	0.0784	+2.3
70	10	30	0.1363	0.1357	-0.44
50	10	30	0.1383	0.1389	+0.43
200	7	80	0.0873	0.0841	-3.6
200	4	80	0.0755	0.0710	-6.3

In this connection it may be pointed out that, as indicated under Preparation of Materials, special tests were conducted to make certain that there were no reducible impurities in the copper solutions, such as iron or arsenic, which would be calculated as copper. Most of the results for copper by this method were low. Additional series of analyses on copper and copper-iron mixtures have shown both the direct

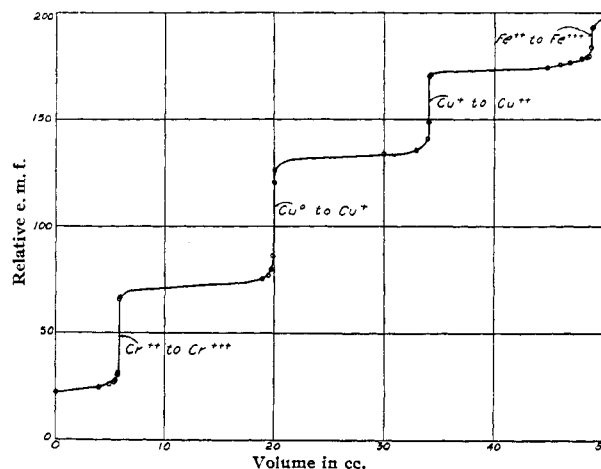


Figure 2—Titration of Copper and Iron by Dichromate after Reduction with Chromous Chloride

and the indirect reductions with titanous chloride alone to be incomplete, so that this solution cannot be used in this connection.

Note—Comment of reviewer of this article: "Failure to make such a correction (that is, for the amount of iron present in the titanous chloride solution itself) could account for the positive errors in Table IV, but not for the negative ones. The fact that exact results were obtained for iron seems to rule out this possible explanation of the high results." The writers did, in fact, find a trace of iron, so small in amount as to have no effect on the results. The variations are, no doubt, inherent in the fundamental titration reaction.

#### Chromous Chloride

The apparent failure of the preceding experiments indicated that selective electrometric titration of the copper and excess reducing agent were probably due to the reduction potentials of both stannous ion and titanous ion being very nearly equal to that of cuprous ion. Therefore an even stronger ionic reducing agent was sought which would make this possible. Chromous, molybdous, and vanadous salts are all powerful reducing agents. Chromous chloride being the most desirable one from the simplicity of its oxidation to chromic ion without intermediate steps, experiments were

carried out as above with marked success. Chromous chloride has a reduction potential (Table I) against hydrogen of +0.43 volts, and it is generally regarded as the most powerful ionic reducing agent. It liberates metallic silver, copper, mercury, lead, and even hydrogen from their ions, and reacts instantaneously with oxygen, for which reason it has been used in gas analysis. The method of preparation and handling of the solution has been given earlier in this paper.

Chromous chloride reduces cupric ion first to cuprous ion, and with the addition of more chromous ion, to finely divided metallic copper. On titrating potentiometrically with dichromate, three inflections are obtained in the e. m. f.-volume curve, corresponding, respectively, to the oxidations  $\text{Cr}^{++}$  to  $\text{Cr}^{+++}$ ,  $\text{Cu}^0$  to  $\text{Cu}^+$ , and  $\text{Cu}^+$  to  $\text{Cu}^{++}$ . The differences of potential between these points are sufficiently great to yield definitely distinguishable inflection points. Several possible reactions may take place during the dichromate titration. For example, metallic copper may be oxidized directly to cupric ion, but the equilibrium constant of the reaction  $\text{Cu}^0 + \text{Cu}^{++} = 2\text{Cu}^+$  is so great that as soon as cupric copper appears it is immediately reduced. Also, if ferrous ion should momentarily be oxidized to ferric, it will at once reverse because of the reaction  $\text{Cu}^+ + \text{Fe}^{+++} = \text{Cu}^{++} + \text{Fe}^{++}$ . Furthermore, if the solution contains iron in addition to copper, another inflection point will be obtained when the ferrous ion is all oxidized (Figure 2). The finely divided sponge copper obtained reacts with surprising rapidity with the dichromate in the hydrochloric acid solution. Under these conditions there is no reaction between ferrous and cupric ions, so that a clean-cut differentiation between iron and copper can be made. Table V shows the results both with copper alone and with copper-iron mixtures.

Table V—Titration of Copper and Copper-Iron Mixtures with Potassium Dichromate after Reduction with Chromous Chloride  
(Approximate initial volume, 50 cc.)

CrCl <sub>2</sub> Cc.	Concd. HCl Cc.	Cu taken Gram	Cu found Gram	Fe taken Gram	Fe found Gram
25	2	0.1075	0.1073	0	0
15	5	0.1115	0.1116	0	0
25	10	0.1256	0.1259	0	0
25	15	0.1224	0.1230	0.1099	0.1098
15	8	0.0790	0.0791	0.1153	0.1153
20	8	0.1087	0.1090	0.1073	0.1075
25	8	0.0974	0.0971	0.0996	0.0996
15	5	0.0784	0.0786	0.0832	0.0834

These results show that the amounts of iron and of copper are reproduced as well by direct potentiometric titration as by any of the standard volumetric methods now in use.

**PROCEDURE FINALLY ADOPTED**—Dissolve the sample of copper ore, matte, or concentrate (0.3 to 0.4 gram according to the nature of material and the concentration of dichromate solution used for titration) in 10 cc. of aqua regia and evaporate to dryness with an excess of concentrated hydrochloric acid to convert all nitrates to chlorides. Take up with a minimum volume of water, add 1 to 2 cc. of concentrated hydrochloric acid, and digest a few minutes to redissolve any basic salts. Filter off the gangue, draining the filtrate into a 200-cc., tall electrolytic beaker. It is desirable to wash by decantation, applying four changes of minimum volumes of water. Add 5 to 10 cc. of concentrated hydrochloric acid, cover with a layer of previously purified kerosene about an inch thick, and add chromous chloride solution until the solution becomes red with suspended, finely divided copper. Add 10 to 15 cubic centimeters of the chromous chloride solution in excess, to make certain of completeness of reduction, as well as to require a sufficient amount of the dichromate so that the first inflection ( $\text{Cr}^{++}$  to  $\text{Cr}^{+++}$ ) can be accurately determined. If the motor stirrer is kept running during this step, the reduction of the copper and iron is very prompt and complete. It is desirable to limit the initial volume of solution titrated to between 50 and 70 cc., as the end points are not quite so sharp at greater dilutions. Titration is then made at room temperature, with dichromate solution. Allow the dichromate to run into the unknown solution at a slow rate, and observe the behavior of the galvanometer of the titration unit. When it gives warning of the approaching inflection

point, take readings at intervals of 0.1 or 0.2 cc., and find the true end point by interpolation instead of by the tedious plotting of curves. The operator can quickly develop skill in detecting the approach and arrival of the inflection point and govern the addition of reagent solution accordingly.

Table VI—Application of Chromous Chloride-Dichromate Method to Determination of Copper and Iron in a Matte

Sample	Initial volume titrated Cc.	CrCl <sub>2</sub> Cc.	Concd. HCl Cc.	Cu present Gram	Cu found Gram	Cu Per cent	Fe present Gram	Fe found Gram	Fe Per cent
0.4360	60	15	1	0.1609	0.1615	36.81	0.1465	0.1467	33.63
0.3627	60	15	5	0.1339	0.1336	36.86	0.1219	0.1223	33.70
0.3226	50	10	8	0.1190	0.1192	36.95	0.1084	0.1081	33.50
0.3138	50	10	10	0.1158	0.1155	36.80	0.1055	0.1053	33.56
0.3229	50	10	2	0.1191	0.1193	36.93	0.1085	0.1086	33.64
Mean per cent copper, 36.87						Mean per cent iron, 33.65			

As far as interfering elements are concerned, magnesium, aluminium, calcium, manganese, zinc, silver, lead, sodium, and potassium would not interfere, and the titration can generally be carried out in the presence of the gangue without filtration, or in the presence of the sulfur which often separates out during dissolution of the sample. Molybdenum, selenium, arsenic, and antimony, which are sometimes present in metallurgical products, might interfere if present in considerable quantity, but could be taken care of readily—as, for instance, by boiling with granulated zinc in acid solution, thus removing the arsenic as arsine, antimony as stibine, etc. The inflections in the curves, which are as a rule strikingly sharp, reproduce the percentages of copper and iron as shown in Table VI and Figure 2.

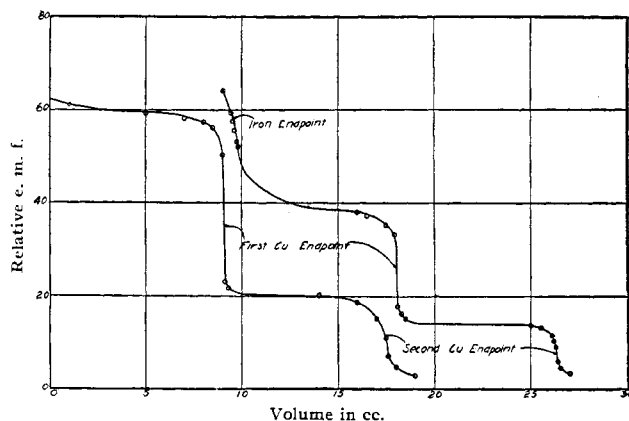


Figure 3—Direct Titration with Chromous Chloride

The samples tested were taken from a composite copper matte prepared under direction of P. P. Butler, superintendent of the Copper Queen Reduction Works of the Phelps-Dodge Corporation at Douglas, Ariz., and had been sent out by him to nineteen smelter chemists of the state to be analyzed for copper, iron, sulfur, etc., so that a comparison of precision of various laboratories as well as of different methods of analysis might be made. He found as a general average of the results the following: copper,  $36.89 \pm 0.1$  per cent; iron,  $33.60 \pm 0.1$  per cent. The results in Table VI are in sufficient agreement to guarantee the reliability of the method. Not only is a great saving of time claimed by this simplified procedure, but also of money, yet preserving the fundamental condition of precision. It is estimated that copper and iron can be determined accurately in less than 50 per cent of the time now required, and in some cases the time has actually been reduced to 25 per cent of what it now takes to obtain accurate results for these elements in any of the metallurgical products, such as mattes, ores, and concentrates. It has not been applied to products very low in copper, such as slags and tailings.

### Direct Titration of Copper and Iron with Standard Reducing Agents

It was considered of interest to attack this problem also from the point of view of direct titration with standard solutions of reducing agents—namely, stannous chloride, titanous chloride, and chromous chloride.

#### Stannous Chloride

As already stated, it appears certain that copper is completely reduced (in the absence of oxygen) by stannous chloride, and the difficulties there cited—namely, that of interaction of cuprous with mercuric ion added for removal of excess stannous, and of the inability to titrate selectively the stannous and cuprous—could be overcome by titrating directly with this reagent. Tenth normal stannous chloride did not give a sufficiently sharp inflection at the end point, so it was decided to employ 0.5 *N* solution, using, of course, correspondingly larger copper samples. This change in concentration of titrating reagent, together with the condition of titrating in hot, concentrated, strongly acid solution, resulted in fair agreement in some instances, but as a rule the results were high, even under rigorous exclusion of atmospheric oxygen. The method was not applied to mixtures of copper and iron for this reason. It is to be noted, however, that reduction is complete when an excess of stannous chloride is used. Table VII gives some of the results of titration with stannous chloride solution.

Table VII—Titration of Copper with Stannous Chloride Solution

Initial volume of soln.	Concd. HCl added Cc.	Temp. C.	Cu present Gram	Cu found Gram	Per cent error
20	10	85	0.4278	0.4308	0.7
20	20	30	0.4171	0.4199	0.7
25	10	85	0.3280	0.3288	0.24
25	10	85	0.3255	0.3330	2.3
30	20	30	0.2098	0.2118	0.95
50	20	85	0.5392	0.5395	0.06

#### Titanous Chloride

Since  $Ti^{+++}$  is 0.14 volt more electropositive than  $Sn^{++}$ , it might be expected that titanous chloride would be found more satisfactory to use in titrating copper directly. Although this is the case, Zintl and Wattenberg<sup>2</sup> find that direct titration cannot be made, and that excess titanous must be present to insure complete reduction. The present writers likewise found this to be true from observations on about twenty-five titrations made under varying conditions of initial volume and volume of concentrated hydrochloric acid added; the results were uniformly high, varying from 1 to 6 per cent. This scheme was therefore abandoned as a possibility of determining copper and iron by direct titration.

*Note*—Kolthoff<sup>3</sup> obtains accurate results for copper and iron by employing potassium thiocyanate or potassium iodate, which are added to the solution after the iron end point is reached in the direct titration with titanous chloride. As the titration proceeds the copper precipitates out as cuprous thiocyanate. Without the use of these reagents, they too fail to obtain satisfactory results by direct titration with titanous chloride.

#### Chromous Chloride

From their experiments with chromous chloride, the writers believed that direct titration would be successful, and found this to be true both in the case of copper alone and in mixtures of copper and iron. The reduction of copper proceeds in steps:  $Cu^{++}$  to  $Cu^+$  and  $Cu^+$  to  $Cu^0$ . If iron is present it is reduced first. In solutions of low acidity<sup>4</sup> these steps are realized electrometrically. Titrations were made in low concentration of hydrochloric acid, acetic acid, and in pres-

ence of excess calcium carbonate. The latter reagents removed the free acid present in the chromous chloride solution remaining from its original preparation. Typical curves are shown in Figure 3, and the results are tabulated in Table VIII. The inflection points in the curves are extraordinarily sharp and permit of an accurate determination of the end point. In most cases interpolation was employed for determining the end points, which saved much of the labor of plotting curves.

Table VIII—Direct Titration of Copper and of Copper-Iron Mixtures by Standard Chromous Chloride Solution

Initial volume Cc.	Acid present	Cu taken Gram	Cu found Gram	Fe taken Gram	Fe found Gram
30	HCl from $CrCl_3$	0.0789	0.0786	0	0
		0.0789	0.0783	0	0
		0.0790	0.0789	0	0
25	HAc-NaAc	0.1122	0.1120	0	0
		0.1208	0.1206	0	0
25	$CaCO_3$ in excess	0.1100	0.1097	0	0
		0.1107	0.1107	0	0
		0.0655	0.0682	0.0636	0.0636
30	HCl from $CrCl_3$	0.0636	0.0656	0.0643	0.0632
		0.0740	0.0771	0.0632	0.0632
30	HAc-NaAc	0.1112	0.1114	0.0958	0.0958
		0.1098	0.1101	0.0967	0.0968
30	$CaCO_3$	0.1109	0.1109	0.1008	0.1007
		0.1021	0.1023	0.1005	0.1005
		0.1110	0.1114	0.1010	0.1009

From these data the writers feel justified in concluding that reduction with chromous chloride under the conditions specified is quantitative. In large volume it was impossible to secure any degree of reproducibility or agreement; in small volume, however, the end points were sharp, but not always in absolute agreement for the two stages of copper reduction, the first being somewhat higher than the second. The first involves the changes  $Cu^{++}$  to  $Cu^+$  and the second,  $Cu^+$  to  $Cu^0$ , the latter of which is very easily discernible to the eye, since the red copper powder separates out. The only explanation they have found for the high result for the first copper inflection is that at this point metallic copper does not begin to separate out until all cupric ions are reduced. The equilibrium  $Cu^0 + Cu^{++} = 2 Cu^+$  must be satisfied. Since copper does not separate out unless a slight excess of chromous ion is present, the additional amount of chromous ion so added is believed to account for the high result. The mean of the two inflection volumes for  $Cu^{++}$  to  $Cu^+$  and  $Cu^+$  to  $Cu^0$  gives the true percentage of copper, and the values so obtained are given in Table VIII.

### Conclusion

In commercial practice it will perhaps be desirable to make reduction with chromous ion and titrate with dichromate, since the latter can more easily be kept at constant normality and also since the chromous chloride is added in excess and its normality need never be definitely known. Inasmuch as this reagent can be so easily prepared from such ordinary reagents as potassium dichromate, arsenic-free zinc, and hydrochloric acid, it can be recommended for smelter laboratory use. The writers have tested its constancy over periods of time, in nearly neutral solution, acid solution, in the presence of rubber, etc., and find it to be a relatively stable, though powerful reducing agent.

**Research on Detonating Silver Compounds**—In connection with the general study intended to develop new uses for silver, research work on detonating silver compounds has been undertaken by the Bureau of Mines. The silver salts that are considered to have explosive properties have been made and tested, and their sensitiveness to heat and impact and explosive strength determined. Experimental work has been conducted with silver azide, silver fulminate, the silver salts of some of the nitroaromatic compounds, and silver oxalate. Work has been completed on silver acetylide and the silver salt of trinitrohydroxyaminobenzene. Other silver compounds were tested but did not have any of the essential properties of an explosive.

<sup>2</sup> Zintl, *Z. Elektrochem.*, **31**, 429 (1925). It is very probable that the reduction potential of chromous ion varies considerably with the hydrogen-ion concentration, as Zintl finds to be true of titanous chloride. See also Kolthoff, *Rec. trav. chim.*, **43**, 772 (1924).