

7. Supposedly divariant equilibria involving iron or ferrous oxide, ferrous oxide or ferro-ferric oxide, water and hydrogen have been studied by only one method which in the hands of different observers yields different results. Possible reasons for these variations are discussed. It is decided that in the present state of the hydrogen system the equilibrium data cannot be used and that more reliable results may be obtained by calculation from the carbon system. Equilibrium constants so calculated are tabulated and compared graphically with the experimental ones.

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[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF THE JOHNS HOPKINS UNIVERSITY]

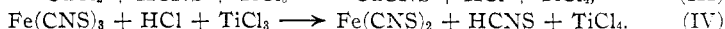
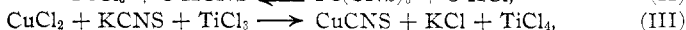
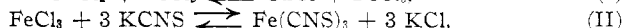
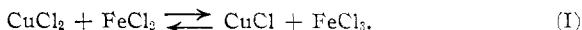
TRIVALENT TITANIUM. II. THE ESTIMATION OF COPPER AND IRON IN THE PRESENCE OF EACH OTHER

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Introduction

The volumetric estimation of copper through the agency of a standard solution of titanous chloride was first made known by Rhead.¹ The copper salt is titrated in the presence of an excess of potassium thiocyanate and a sufficient quantity of iron (all of which must be in the ferrous condition) until the red color of ferric thiocyanate just disappears. The following equations will serve to make the matter clear.



Moser,² in turn, has studied this determination and has found it possible to dispense with all indicators, relying solely upon the color of the cupric salt itself. Monnier,³ however, employs certain dyestuffs, *viz.*, safranin or indulin, as indicators. Mach and Lederle⁴ have in like manner investigated the subject. Finally, Knecht and Hibbert,⁵ besides giving Rhead's procedure, make use of the alternate plan of adding a measured amount of standard ferric ammonium sulfate and subsequently deducting its equivalent in terms of the titanous chloride solution, the titer thus corrected being proportional to the copper only.

Regarding the determination of copper when accompanied by iron, Rhead¹ dismisses the case by saying that the iron may be removed as

¹ Rhead, *J. Chem. Soc.*, **89**, 1491 (1906).

² Moser, *Chem.-Ztg.*, **36**, 1126 (1912).

³ Monnier, *Ann. chim. anal.*, **21**, 109 (1916).

⁴ Mach and Lederle, *Landw. Vers. Sta.*, **90**, 191 (1917).

⁵ Knecht and Hibbert, "New Reduction Methods in Volumetric Analysis," Longmans, Green and Co., 1918, pp. 13 and 55.

acetate. This cannot be taken as a felicitous suggestion; since experiments by Brearley,⁶ which are also cited by Ibbotson,⁷ on the separation of iron from other metals by differential hydrolysis of the acetates, go to show that of the 5 metals, manganese, zinc, cobalt, nickel and copper, the last is freed from iron with the greatest difficulty.

Knecht and Hibbert⁸ precipitate the copper with hydrogen sulfide, and oxidize the iron in the filtrate with a mixture of ammonium hydroxide and hydrogen peroxide. After acidifying, the iron is determined by titrating with titanous chloride in the ordinary way. In a separate portion of the sample the copper and iron are estimated together. Although this process would undoubtedly yield accurate results, it has the disadvantage of being rather troublesome and lengthy.

Monnier,⁹ however, resorts to the novel expedient of titrating one aliquot part of the test solution with titanous chloride using methylene blue as indicator, which gives the iron alone, and treating another part similarly but with either safranin or indulin as indicator, the second titer representing the sum of the copper and the iron.

In considering the above methods, it occurred to the writer that the problem of analyzing a mixture of copper and iron might be solved in an extremely simple way. If, after having titrated the two metals (in the form of their sulfates) with titanous sulfate in the presence of a soluble thiocyanate, the cuprous thiocyanate should be eliminated by filtration, then the iron could be determined in the filtrate by titration with potassium permanganate after the addition of sufficient silver nitrate to precipitate the thiocyanic acid.¹⁰

Experimental

Known amounts of copper and iron, in the form of cupric and ferric sulfates, respectively, were taken in solution of small bulk, preferably less than 100 cc. Ten cc. of 1:1 sulfuric acid¹¹ was added and the liquid cooled with running water to 15°; whereupon, after introducing ammonium thiocyanate,¹² the first titration was accomplished by means of a standard solution of titanium trisulfate, the disappearance of the pink color being

⁶ Brearley, *Chem. News*, **75**, 253 (1897); **76**, 49, 165, 175, 210, 222 (1897).

⁷ Ibbotson, "The Chemical Analysis of Steel-Works' Materials," Longmans, Green and Co., 1920, pp. 7 and 90.

⁸ Ref. 5, p. 56.

⁹ Ref. 3, p. 113.

¹⁰ Cf. Edgar, *THIS JOURNAL*, **38**, 884 (1916).

¹¹ Van Name, *Am. J. Sci.*, [4] **10**, 451 (1900), has shown that cuprous thiocyanate is practically insoluble in solutions containing up to 12% of conc. sulfuric acid by volume, but that precipitation is delayed when much acid is present. In the present instance it would seem that the acid concentration may vary within reasonable limits.

¹² From 2.5 to 5 cc. of a 10% ammonium thiocyanate solution was used depending upon the quantity of copper expected.

taken as the correct end-point. The whole was then heated to incipient ebullition to coagulate the precipitate, cooled somewhat, filtered and washed with cold water. The filtrate was cooled to 15° and the red color, which will have inevitably returned to some extent, bleached out by the very careful addition of the titanium solution (this extra portion being of course neglected). The solution was cooled still further and, after the introduction of enough silver nitrate¹³ to precipitate all the thiocyanate, but without filtering off the precipitate of silver thiocyanate, the second titration was made with standard potassium permanganate.

The accompanying table of experimental results, wherein the relative amounts of copper and iron were greatly varied, is deemed sufficient to show that, in the main, the process has a fair claim to accuracy

TABLE I
TEST ANALYSES

Expt.	Copper taken G.	Copper found G.	Copper error G.	Iron taken G.	Iron found G.	Iron error G.
1	0.0640	0.0634	-0.0006	0.0475	0.0478	+0.0003
2	0.1275	0.1273	-0.0002	0.0095	0.00935	-0.00015
3	0.0277	0.0280	+0.0003	0.0760	0.0760	0.0000
4	0.0259	0.0258	-0.0001	0.0665	0.0666	+0.0001
5	0.0355	0.0355	0.0000	0.0855	0.0859	+0.0004
6	0.0398	0.0403	+0.0005	0.0760	0.0760	0.0000
7	0.0120	0.0129	+0.0009	0.0950	0.0945	-0.0005
8	0.2545	0.2532	-0.0013	0.0095	0.00905	-0.00045
9	0.1590	0.1578	-0.0012	0.1399	0.1391	-0.0008
10	0.1590	0.1588	-0.0002	0.0280	0.0274	-0.0006

Notes and Precautions

It is important to examine the titanium reagent scrupulously for iron and to apply the proper correction later when calculating the iron content of the material being analyzed. This can easily be done by the method of Newton.¹⁴

Since both end-points must be obtained in the presence of white precipitates, either of which may be of considerable magnitude, some difficulty is likely to be experienced in ascertaining the points of complete reaction. Such obstacles, however, tend to diminish with practice. In case the material to be analyzed runs very high in copper and very low in iron, it is advisable to add an accurately measured volume of standardized ferric ammonium sulfate and then deduct its value from both titrations. This will enhance the delicacy of the first color indication without reducing appreciably the exactness of the process. For sharpness of the

¹³ A 25% solution of silver nitrate was used in conjunction with the 10% ammonium thiocyanate, volume for volume.

¹⁴ Newton, *Am. J. Sci.*, [4] 25, 343 (1908).

second end-point, small volume and low temperature and good daylight are the desired conditions.

All titrations herein recorded were performed in air, the chief reason for this being that the method would thus prove more convenient in technical analysis. The small losses of trivalent titanium due to atmospheric oxidation, as noted in a previous communication,¹⁵ were assumed to be approximately offset by making the standardization experiments in the air also.

Summary

A differential volumetric process has been worked out for the estimation of both copper and iron in admixture, which depends upon the following principles.

1. The two metals, in the form of their sulfates, may be titrated in the presence of a soluble thiocyanate with a standard titanous sulfate; the titer corresponds to the sum of the copper and the iron.
2. The coagulated precipitate of cuprous thiocyanate produced in the first titration may be completely removed by filtration.
3. The small amount of ferric sulfate formed as the result of atmospheric oxidation may be reduced to the ferrous condition by the addition of an extra portion of titanous sulfate.
4. The thiocyanate may be rendered inactive toward permanganate by the introduction of silver nitrate in excess, whereupon the titration for iron may be carried out notwithstanding the presence of silver thiocyanate.
5. The titanium trisulfate must be tested for iron and the proper correction applied in case an appreciable quantity is found.

The greater part of the experimental work set forth above was executed in the laboratory of the School of Chemistry of the University of Minnesota. It is a pleasure, therefore, to thank Dean Lauder W. Jones¹⁶ for encouraging the research as well as Dr. L. H. Reyerson, through whose efforts the writer enjoyed the privileges of the University of Minnesota during the summer of 1920 in the capacity of Research Fellow by Courtesy.

Moreover, the writer wishes to express his indebtedness to Mr. Frank I. LaMotte¹⁷ for the gift of a liberal specimen of titanous sulfate, with which the latter part of the work was done. It was found to be virtually free from iron so that the correction previously mentioned became zero.

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¹⁵ Thornton and Chapman, *THIS JOURNAL*, **43**, 91 (1921).

¹⁶ Now of Princeton University.

¹⁷ LaMotte Chemical Products Company, 13 West Saratoga Street, Baltimore, Md.