be regarded as a bromine derivative of the neutral or β-modification of the diketone, anisoyl benzoyl methane.

We expect to continue this work in various directions, and to extend the investigations to other analogously constituted compounds.

A NEW VOLUMETRIC METHOD FOR THE ESTIMATION OF COPPER.

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EXPERIMENTS looking to the use of the thiocyanates in volumetric processes have been carried on in this laboratory for over two years past. While the results obtained are in many ways very satisfactory, it is intended here to make note of one application, which gives results of great practical value.

The iodine and cyanide methods for the estimation of copper are far from satisfactory. Two methods, recently proposed in this Journal,[1] making use of the precipitation of copper as cuprous thiocyanate, mark a decided advance in methods. It is believed that the process here outlined has further points of advantage. It involves the precipitation of the copper as cuprous thiocyanate, the oxidation of the copper without decomposition of the alkali thiocyanate and the titration of the acidified thiocyanate with standard permanganate. In practice the two latter steps are one operation, but one filtration is necessary and for most ores thirty to forty minutes are ample for a determination from the time of weighing the sample to the time of the final titration.

Some attention must be given to the condition of the solution before precipitating the copper as cuprous thiocyanate. If the solution contains free sulphuric acid it should not exceed 1 or 2 per cent. in amount. Stronger solutions on heating with thiocyanate have a tendency to liberate free sulphur which remains with the precipitate and in the final reading gives variable results. The same thing is true regarding hydrochloric acid. With nitric acid no free sulphur is liberated. Here, however, an excess of acid prevents the reduction and complete pre-

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[1] This Journal, 19, 940 (1899) and 20, 610 (1900).

cipitation of the copper, so that in any case an amount of free acid in excess of 1 or 2 per cent. is to be avoided. Since the greatest safety seems to reside with the nitric acid it is preferred. This is an advantage also for in the initial treatment of mattes, ores, etc., it avoids the necessity of evaporating the solution to sulphuric acid fumes for the removal of the nitric acid. Further it may be noted that a small amount of sulphuric acid, resulting from the action of strong nitric acid or otherwise present, does not interfere with the precipitation. The reduction of the copper is best effected by a strong solution of sulphur dioxide, a few cc. being added from time to time. A 10 per cent. solution of sodium sulphite may be similarly used but it is better not to add acid to such a solution to liberate the sulphurous acid but allow it to be liberated by the free acid of the copper solution. The next point to be observed is the addition of the alkaline thiocyanate. The precipitated cuprous thiocyanate is very appreciably soluble in an excess of this reagent. Two cc. of a 10 per cent. solution of potassium thiocyanate will precipitate several times the amount of copper that could be conveniently handled in the subsequent titration; hence, that amount of reagent is sufficient to use, and at the same time there is no danger of re-solution of the precipitate. This reagent may be added with the reducing agent, before or after it, seemingly without preference. Heating on a water-bath or hot plate with stirring should be continued till the separation of the precipitate is complete and the supernatant liquid becomes perfectly clear. This requires from five to ten minutes.

The filtration is best made on a thick asbestos felt well packed in a 1½-inch porcelain filter funnel using a pump. A felt ⅛ inch or more thick should be used. The washing which should be made with hot water is complete when the filtrate, upon acidifying, will not decolorize a drop of permanganate. Special care should be taken that none of the precipitate passes through with the filtrate. The filter with the asbestos-pulp is returned to the beaker, 2 or 3 cc. of caustic soda (10 per cent.) solution are added, well stirred and warmed to 60° or 70°. The mixture after a few minutes is ready for titrating with the standard permanganate, the object being first to add to the alkaline mixture the amount of permanganate needed to oxidize the cuprous hydroxide formed from the addition of the alkali, then to acidify and proceed with the rest of the titration to oxidize the thiocyanic acid. The first part of the reaction, that which takes place in the alkaline condition, is confined to the copper so long as any cuprous hydroxide remains. The following equation represents the change taking place:

$$8\mathrm{CuOH} + \mathrm{K_2Mn_2O_8} + 8\mathrm{H_2O} = 2\mathrm{KOH} + 8\mathrm{Cu(OH)_2} + \mathrm{Mn_2(OH)}.$$

Now it is not necessary that at the exact end of this reaction on the copper the change should be made to the acid condition, but it is necessary that this point be fully passed in order that upon acidifying there may not be reprecipitated some cuprous thiocyanate. Fortunately it is easy to tell when this point has been passed, and in this way, when the copper has been all oxidized there begins a reaction between the alkaline thiocyanate and the permanganate which results in the formation of the green manganate thus:

$$4\mathrm{K_2Mn_2O_8} + \mathrm{NaCNS} + 10\mathrm{NaOH} = 4\mathrm{K_2MnO_4} + 4\mathrm{Na_2MnO_4} + \mathrm{NaCNO} + \mathrm{Na_2SO_4} + 5\mathrm{H_2O}.$$

It will be seen, therefore, that the bright yellow of the cuprous hydroxide becomes more and more mixed with the dark brown of the $\mathrm{Mn_2(OH)_6}$ and soon fails to give any yellow tint whatever; further addition of permanganate produces a decided green tint to the liquid part of the mixture. If after a minute or two this remains permanent it may be known that all the copper has been oxidized.

Dilute sulphuric acid (1 : 5) is now slowly added with constant stirring to prevent heating. When the solution becomes clear a decided excess of the dilute acid is added, the whole warmed to 60° or 70°, and the titration continued to the usual pink end reaction. If in this part of the reaction the brown manganic hydroxide does not quickly disappear by solvent action of the acid, it is evidence that the acid is not present in sufficient excess or that the amount started with has been largely exhausted and more acid should be added. Concentrated acid may not, at any time, be added to the solution because of the tendency to form the carbon oxysulphide.

Notwithstanding the above somewhat roundabout reactions, the whole process proceeds uniformly as if the reaction were simply thus: $10CuCNS + 7K_2Mn_2O_8 + 21H_2SO_4 = 7K_2SO_4 + 14MnSO_4 + 10HCN + 10CuSO_4 + 16H_2O$. This reaction serves to emphasize two things: first, that much sulphuric acid is needed in the reaction, and second, that the amount of permanganate used is high in proportion to the copper present.

This is further evident when it comes to the matter of calculation. In determining the permanganate factor for copper from its iron standardization it is noted that by the above equation the molecular ratios are: $10Cu : 7K_2Mn_2O_8$. Comparing with the usual iron ratio 1 : 10, we find the ratio between copper and iron to be $10Cu : 70Fe$ or 63.6 : 392 or 0.1602. Hence the iron value per cubic centimeter of the permanganate multiplied by the factor 0.1602 will give the copper value per cubic centimeter. While this feature is an advantage where the copper content is low, it also calls for the use of small quantities where the copper content is high, otherwise the consumption of permanganate will be excessive. It is therefore best to weigh out 1 gram of the substance and make up to 250 or 500 cc., and take an aliquot part as seems to be indicated by the depth of color due to the copper present. A decinormal solution of permanganate having an iron factor of 0.0056 would have a copper factor of 0.000897; hence, an amount of copper in excess of 40 milligrams would use more than 50 cc. of permanganate.

It may be well to note further that the amount of permanganate used in oxidizing the copper is only about one-sixth of the amount used in subsequent titration; hence, there is little danger of overrunning the total amount in the alkaline part of the process where the end reaction is indefinite. This point is further illustrated by the equation for thiocyanic acid alone, thus:

$$10HCNS + 6K_2Mn_2O_8 + 8H_2SO_4 = 6K_2SO_4 + 12MnSO_4 + 10HCN + 8H_2O.$$

The process evidently demands that the thiocyanate precipitate be very complete, exact and free from sulphur. That these conditions are easily attainable seems to be indicated by the results. Removal of other metals is not necessary, even silver does not interfere because unaffected by the treatment with caustic alkali, and the insoluble silver thiocyanate acts so very slowly on permanganate solution as not to vary the end-reaction appreciably. Results have been obtained as follows:

A solution of copper sulphate was made and acidified with nitric acid. Careful electrolytic determination of the copper gave a factor for each cubic centimeter of 0,00661 gram.

	Solution taken. cc.	Titration. cc.	Indicated copper in mg. per cc.	Error as referred to electrolytic result in mg. per cc.
(*a*)	5	32.8	6.63	+0.02
(*b*)	5	32.6	6.59	—0.02
(*c*)	5	32.8	6.63	+0.02
(*d*)	5	32.5	6.57	—0.04
(*e*)	5	32.7	6.60	+0.01
(*f*)	10	65.6	6.63	+0.02
(*g*)	20	130.6	6.59	—0.02
(*h*)	40	372.0	6.60	—0.01

The reaction between a thiocyanate and permanganate seems to be very constant. One exception only has been found and that not necessarily of such a nature as to interfere with the accuracy of the above process.

A solution of 1.5 grams of ammonium thiocyanate to a liter of water has a strength very nearly corresponding to N/10 permanganate solution. Now up to this point of dilution the thiocyanate seems to react regularly and in accordance with the above reactions. If, however, the thiocyanate be largely diluted beyond this point, the amount of permanganate used up in the reaction is appreciably less than the same quantity of thiocyanate would use, if undiluted. For example, a measured quantity, say 10 cc., of thiocyanate, if diluted 200 times, will titrate approximately 0.1 cc. of N/10 permanganate less than the same solution would use if undiluted.

This tendency to a lower titration seems to be corrected by acidifying more strongly with acid to correspond with the dilution; also in a less degree by somewhat higher heat.

Such possibility of error, however, is easily guarded against by keeping the solution of copper and thiocyanate in a concentrated form, or rather refrain from diluting the mixture, the necessary reagents alone furnishing all needed dilution from the time of treating the asbestos pulp and precipitate with alkali to the final titration with the permanganate. I desire to acknowledge my obligation to Mr. A. R. Johnston for the analytical data connected with this work.

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