3. Other conditions being constant, the composition of these basic sulfates is independent of the temperature of preparation within the range investigated.

4. The evidence obtained by a study of these salts makes it seem highly probable that they are not definite compounds, but rather are to be regarded as a three-component system in which all three components, $CuSO_4$, CuO and H_2O (or if one prefers CuO, SO_3, H_2O) are continuously variable within certain limits.

5. The evidence indicates that the maximum number of molecules of copper oxide that are capable of being taken up by one of copper sulfate is two, and that the formula for the most basic salt is probably quite close to $CuSO_4.2CuO.2H_2O$.[1]

6. In salts of lower basicity the water content of the salt increases as the copper oxide content decreases, but there is as yet no evidence to show whether these changes continue throughout the whole range to normal $CuSO_4.5H_2O$.

7. Basic copper sulfates prepared by heating copper sulfate and water together in varying relative amounts does not lead to the formation of definite compounds as has been maintained.

8. There is some evidence indicating the formation, under undetermined conditions, of a metastable series of basic sulfates.

9. In view of the above facts, it is only natural that the mineral Brochantite, should show a variable composition, depending on the conditions of its formation.

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY OF THE UNIVERSITY OF KANSAS.]

CHLORIDES IN PRESENCE OF THIOCYANATES.

BY F. W. BRUCKMILLER.

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Rosanoff and Hill[2] have shown that chlorides can be determined in the presence of thiocyanates by means of Volhard's method after the latter have been decomposed by concentrated nitric acid. This paper intends to show that chlorides can also be titrated with silver nitrate and chromate

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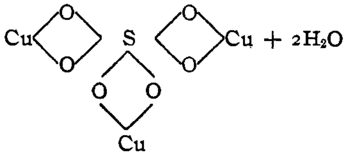
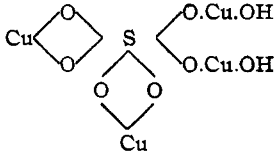
[1] Professor W. A. Noyes has kindly called the authors' attention to the fact that this formula corresponds to that of the normal copper salt of orthosulfuric acid, $S(OH)_6$, with two molecules of water of crystallization, and may be written



or if one prefers



[2] THIS JOURNAL, 29, 1467 (1907).

indicator after the thiocyanates have been decomposed with nitric acid. Such a method is useful in water analysis where chlorides and thiocyanates occur together and it is desired to know only the chlorine content.

The solution containing the chlorides and thiocyanates is heated to boiling and concentrated nitric acid added drop by drop, the amount depending upon the thiocyanate present. If present in large quantities, nitric acid is added until the solution turns a light brown. For small quantities 2–3 cc. of nitric acid are sufficient. The solution is boiled for 15 minutes and filtered if necessary (free sulfur being precipitated if the concentration of thiocyanate is large) and after cooling is neutralized with normal $NaHCO_3$, using methyl orange as indicator. A little more than enough for neutralization is added, and after adding 1 cc. of chromate indicator, silver nitrate is added to the usual end point.

The method assumes (1) that the thiocyanate may be decomposed at 100° by such quantities of HNO_3 as are insufficient to oxidize the chloride or cause volatilization of HCl; (2) that all but traces of hydrocyanic acid formed during decomposition can be volatilized during the time required for oxidation; (3) that the sulfur is not present in such a form as to react with the $AgNO_3$; (4) that the color of the methyl orange indicator does not interfere with the chromate end point.

Rosanoff has shown that no chlorine is lost as such, or as hydrochloric acid, in boiling the solution with nitric acid, and we have been able to confirm his conclusions. Varying amounts of sodium chloride were taken and boiled with varying quantities of nitric acid, and the solutions analyzed for chlorine before and after. The results in Table I show that no chlorine was lost during the operation.

TABLE I.—EFFECT OF NITRIC ACID ON SODIUM CHLORIDE SOLUTION AT 100°.

Cc. HNO_3.	1.	2.	3.	4.	5.
		Volume 100 cc.			
NaCl before	0.0150	0.0150	0.0150	0.0150	0.0150
NaCl after	0.0149	0.0150	0.0151	0.0148	0.0148
		Volume 50 cc.			
NaCl before	0.0150	0.0150	0.0150	0.0150	0.0150
NaCl after	0.0148	0.0149	0.0148	0.0151	0.0151
		Volume 25 cc.			
NaCl before	0.0150	0.0150	0.0150	0.0150	0.0150
NaCl after	0.0150	0.0148	0.0147	0.0147	0.0147

In the decomposition of thiocyanate, hydrocyanic acid is one of the principal decomposition products. In pure solutions it is all removed by boiling, but in presence of chlorides a small quantity is always retained. In no case, however, was this amount larger than 3 mg. of CN per liter. This is not in accord with the work of Richards and Singer,[1] who find that larger quantities are retained. The complete removal

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[1] *Am. Chem. J.*, 27, 208 (1902).

of the hydrocyanic acid is desirable, but traces do not interfere with the accuracy of the method. Even if 3 mg. per liter were always retained, the error in titrating chlorides in water analysis would be only 3 parts per million.

During decomposition the sulfur does not form any compound which in any way interfere with the titration with silver nitrate. No hydrogen sulfide was ever detected. Free sulfur forms if the concentration of thiocyanate is large. The exact products resulting were not determined, but, besides free sulfur, they are probably sulfate and complex organic compounds.

The presence of methyl orange in the solution gives a little different shade to the end point with chromate indicator but it is as easily duplicated and detected as is the color obtained in absence of methyl orange. Solutions of sodium chloride were titrated in presence and in the absence of methyl orange with the following results:

$AgNO_3$ with methyl orange (cc.)......	15.05	20.00	50.10	100.20
$AgNO_3$ without methyl orange (cc.)...	15.00	19.98	50.00	100.12

The solution is neutralized with sodium bicarbonate, instead of sodium hydroxide, to guard against an excess of hydroxyl ion in the solution with which silver nitrate reacts. An end point with the chromate indicator is obtained in a slightly acid solution but if considerable acid is present no end point is obtainable. The maximum concentration of (H^+) allowable was determined and the results included in Table II.

To several solutions containing known quantities of chloride were added varying concentrations of sulfuric acid, beginning with 0.0004 *N*. Fifty cc. of each of these were titrated for chlorides according to the usual procedure.

TABLE II.—EFFECT OF ACID ON TITRATION OF CHLORIDES.

Conc. of H_2SO_4 mols.	Grams of Chlorine per Liter.							
	Present.	Found.	Present.	Found.	Present.	Found.	Present.	Found.
0.0002	0.026	0.026	0.084	0.084	0.104	0.104	0.206	0.206
0.0060	0.026	0.026	0.084	0.084	0.104	0.104	0.206	0.206
0.0010	0.026	0.026	0.084	0.084	0.104	0.104	0.206	0.206
0.0012	0.026	0.026	0.084	0.084	0.104	0.104	0.206	0.206
0.0014	0.026	0.026	0.084	0.084	0.104	0.104	0.206	0.206
0.0016	0.026	[1]	0.084	[1]	0.104	[1]	0.206	[1]

These results indicate that chlorides can be determined by titration in a 0.0014 *M* solution of sulfuric acid or a concentration of 0.0028 (H^+), assuming that all of the acid is dissociated.

From these results we conclude that by decomposing the thiocyanates with hot nitric acid, chlorides can be determined volumetrically, using silver nitrate and chromate indicator.

LAWRENCE, KANSAS.

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[1] No end point possible.