

It will be seen that the results obtained by the volumetric method coincide very well with those obtained by the gravimetric method. It will therefore appear that this method is perfectly safe to use for rapid accurate work.

Note.—Owing to a number of errors in bibliography, the following corrections are given below :

Stolba, Zur quantitativen Bestimmung der Magnesia, Phosphor und Arsen durch Alkalimetrie. Chem. Zentr., 1876, 727 instead of 1866.

R. K. Meade, A New Volumetric Method for Magnesium. J. Am. Chem. Soc., 1899, p. 146, instead of 1889. (See Sutton's Volumetric Analysis).

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THE DETERMINATION OF CHLORIDES OR BROMIDES IN THE PRESENCE OF SULPHOCYANATES.¹

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§ I. Introductory.

In the course of a research undertaken in this laboratory it became necessary to analyze a number of solutions containing mixtures of chlorides and sulphocyanates. Investigation of the literature of the subject showed that no method exists by which such mixtures can be analyzed quickly and accurately; it was found that those methods which can be relied upon for accuracy of results require such expenditure of time as prohibits their use where large numbers of analyses must be performed. In like manner search revealed no suitable method for the analysis of bromide-sulphocyanate mixtures.

To remedy this lack, the following volumetric method is proposed. It permits of an accuracy within the limits of the usual errors of measurement with pipettes and burettes, and requires less time than any of the existing methods; a single complete determination has been found to require about one and one-half hours, while two determinations can be performed without difficulty in two hours. By proper organization of the work eight to ten analyses can easily be made within a working day.

The sum of chloride and sulphocyanate, or of bromide and sulphocyanate, is established by precipitation with excess of standardized silver nitrate and determination of the excess by titration with standardized ammonium sulphocyanate, according to the method of Volhard.² Precipitates containing silver chloride must be filtered off before the excess of silver nitrate is determined, while in the case of the bromide filtration is unnecessary.³ The new method has for its object, the determination of the chloride or bromide in a fresh sample of the solution, by oxidizing

¹ Presented before the New York Section of the Am. Chem. Soc., May 10, 1907.

² J. pr. Chem., 9, 217 (1874); Z. anal. Chem., 13, 171, (1874).

³ Rosanoff and Hill. This Journal, 29, 269, (1907); Chem. Zentr., 1907, I, 1596.

the sulphocyanate to hydrocyanic acid by means of nitric acid, expelling nearly all the hydrocyanic acid, and determining the residual chloride or bromide, in the presence of the traces of cyanide, by the Volhard method. The sulphocyanate originally present is found by difference.

§ 2. Determination of Chlorides.

The following solutions are required: (*a*) a fifteenth-normal solution of silver nitrate, standardized gravimetrically or by weight of silver nitrate used; (*b*) a fifteenth-normal solution of ammonium sulphocyanate, standardized against the silver nitrate by Volhard's method; (*c*) a saturated solution of iron-ammonium alum, free from chlorides and treated with nitric acid to lighten the color.

A measured volume of the chloride-sulphocyanate mixture is diluted so that the normality of the chloride is about one-fiftieth. The solution is treated with 1 cc. of the iron-ammonium alum and brought to a boil in a large Erlenmeyer flask. To the gently boiling solution concentrated nitric acid is added at the rate of about three drops a minute, during which operation the liquid should be frequently stirred to prevent super-bullition. The addition of the acid in the above described manner is continued until the color of the solution has faded to a *pale orange*, and then without further addition of acid the solution is allowed to boil for a few minutes longer, by which treatment the last traces of sulphocyanate are oxidized. The complete oxidation requires about twenty minutes time; a change of color to pure yellow indicates the completion of the operation. The odor of hydrocyanic acid is now practically gone.

Cool the solution thoroughly under the tap and add to it one-third its volume of concentrated nitric acid. Add a measured amount of N/15 silver nitrate in moderate excess above the quantity required to precipitate the chloride and shake the mixture until the precipitate is well coagulated, which requires but a few minutes' agitation when the solution is cool, but *a much longer time if the solution is heated*. When the precipitate is well coagulated bring the solution again to a gentle boil, maintaining it at this temperature for about five minutes. The liquid above the precipitate must become perfectly clear.

Filter the solution while still hot through a rapid-running double filter, paying no attention to the opalescence which forms in the filtrate upon cooling. Wash the precipitate with hot water containing a few drops of nitric acid. Allow the liquid to cool thoroughly, dilute until the volume is about three times that of the solution before filtration, add 2 cc. of the iron indicator for every 100 cc. of solution and run in the standardized sulphocyanate to a strong red color. Stir the solution for five minutes and then add the standardized silver nitrate drop by drop, with stirring, until

the color just disappears. A single drop of the sulphocyanate solution should then give a permanent pink color; should it fail to do so, titrate back and forth with the silver nitrate and ammonium sulphocyanate until the color changes on addition of a single drop. The titration is best conducted in a porcelain dish, against the white ground of which the end-point is most accurately determined; in glassware transmitted light effects may be misleading. The total silver nitrate added, *minus* the total ammonium sulphocyanate added, is the silver nitrate equivalent of the chloride present.

The following is a list of ten consecutive analyses of mixtures of potassium chloride and sulphocyanate performed according to the foregoing directions:

	N/15 KCl solution in cc.	N/15 KCNS solution in cc.	AgNO ₃ equivalent of KCl taken	AgNO ₃ equivalent found	Absolute error in cc.
1.	0.00	25.00	0.00	0.02	+0.02
2.	10.00	90.00	9.95	9.96	+0.01
3.	25.00	50.00	24.87	24.87	±0.00
4.	25.00	50.00	24.87	24.86	-0.01
5.	25.00	25.00	24.87	24.88	+0.01
6.	25.00	25.00	24.87	24.93	+0.06
7.	25.00	10.00	24.87	24.83	-0.04
8.	25.00	5.00	24.87	24.90	+0.03
9.	25.00	3.00	24.87	24.84	-0.03
10.	25.00	0.15	24.87	24.90	+0.03

§ 3. Determination of Bromides.

The analysis of bromide-sulphocyanate mixtures is conducted precisely as that of the chloride mixtures, with three modifications: (*a*) the solution to be treated with nitric acid for the destruction of the sulphocyanates should be diluted to roughly one-hundredth normality with respect to bromides; (*b*) after the sulphocyanate has been decomposed at the boiling temperature and the liquid thoroughly cooled, only one-sixth its volume of concentrated nitric acid is added; (*c*) the precipitated silver salts should not be filtered off before the excess silver nitrate is determined.

The following analyses of bromide-sulphocyanate mixtures were made according to the above directions:

	N/15 KBr solution in cc.	N/15 KCNS solution in cc.	AgNO ₃ equivalent of KBr taken	AgNO ₃ equivalent found	Absolute error in cc.
1.	25.00	0.15	22.72	22.76	+0.04
2.	25.00	0.15	22.72	22.69	-0.03
3.	25.00	3.00	22.72	22.73	+0.01
4.	25.00	5.00	22.72	22.78	+0.06
5.	25.00	10.00	22.72	22.69	-0.03
6.	25.00	10.00	22.72	22.68	-0.04
7.	25.00	25.00	22.72	22.73	+0.01
8.	25.00	50.00	22.72	22.74	+0.02
9.	25.00	100.00	22.72	22.72	±0.00
10.	10.00	90.00	9.09	9.12	+0.03

§ 4. Theory of the Method.

While the best test of a method is in its practical results, it is well to establish clearly the facts upon which it is based. Our method depends upon the following assumptions: (1) that sulphocyanates may be decomposed at a temperature of about 100° by such concentrations of nitric acid as are insufficient either to oxidize chlorides or bromides or to cause the volatilization of hydrochloric or hydrobromic acid; (2) that all but traces of the hydrocyanic acid formed by this decomposition can be volatilized during the time required for the oxidation itself; (3) that the silver cyanide formed by addition of silver nitrate to this solution is sufficiently soluble in hot nitric acid to be separated quantitatively from the insoluble silver chloride by filtration; and finally, (4) that small amounts of silver cyanide do not interfere with the determination of the excess of silver by means of a sulphocyanate titration, since it acts as a soluble silver salt. Each of these assumptions has been subjected to experimental investigation.

The quantity of concentrated nitric acid used during the oxidation ordinarily amounts to 2 cc. or less. If acid should be added more rapidly than the decomposition of the sulphocyanate required, there can be present at any time not more than this small amount of acid in solutions the volume of which is usually about 200 cc. Experiments were therefore conducted to ascertain whether this amount of nitric acid could be used without loss of chlorine or bromine from solutions of the concentration used in our analytical method. 200 cc. samples of N/50 chloride solution, or N/100 bromide solution, were boiled gently for fifteen to twenty minutes with varying amounts of concentrated nitric acid, and the distillates, amounting in each case to about 15 cc., were carefully tested for the presence of the halogens. The experiments tabulated below were performed in duplicate:

N 50 KCl in cc.	Conc. HNO_3 in cc.	Vol. of distillate in cc.	Cl present.
200	1.00	15	None
200	2.00	15	None
200	3.00	15	None
200	4.00	15	None
200	6.00	15	Traces
N/100 KBr in cc.	Conc. HNO_3 in cc.	Vol. of distillate in cc.	Br present.
200	1.00	15	None
200	2.00	15	None
200	3.00	15	None
200	3.50	15	Traces

The results show that under the conditions of analysis, loss of halogen cannot be caused by the addition of nitric acid and boiling.

The principal, but by no means the only, decomposition product of sulphocyanic acid is hydrocyanic acid. Tests showed that when a pure sulphocyanate is decomposed in the manner described, only traces of

hydrocyanic acid remain in the solution ; when the decomposition is carried out in the presence of a chloride, amounts are retained corresponding to less than two milligrams of silver cyanide. This rapid loss of hydrocyanic acid during twenty minutes' treatment appeared somewhat surprising in the light of Richards and Singer's¹ observation that the presence of chlorides prevents the expulsion of hydrocyanic acid to a marked extent. It occurred to us therefore that the decomposition of the sulphocyanate might possibly result in the formation of cyanogen rather than hydrocyanic acid, as was suggested by Knüpfner², who oxidized the sulphocyanate with acid potassium iodate. Accordingly, the decomposition products were passed through a solution of potassium hydroxide and the alkaline liquid analyzed; it was found to contain cyanide but no cyanate, showing the absence of cyanogen and indicating that we had in reality to do with a very rapid expulsion of hydrocyanic acid. Richards and Singer³ expressed the view that the retention of the hydrocyanic acid by chlorides might be due to the formation of ionic complexes. Assuming this interpretation to be correct, it would appear that the complex requires a measurable time interval for its formation, and that boiling will expel hydrocyanic acid from chloride mixtures much more rapidly at the time of its formation than after the solution has been allowed to stand. It would in all probability, be a lengthy operation to volatilize the acid quantitatively, but this is unnecessary in connection with our method.

The solubility of silver cyanide in nitric acid of moderate strength, which is taken advantage of in our method of analysis, was noted by Gregor⁴, who showed the marked solubility of the cyanide in 6—10 per cent. acid. In hot solutions of 25 per cent. strength we find its solubility much greater; at 80° about 0.5 cc. of N/15 potassium cyanide and 0.5 cc. of N/15 silver nitrate, corresponding to about 4 mg. of silver cyanide, can be added to 200 cc. of the acid without causing any turbidity. The amount of hydrocyanic acid left in the solution in our method is considerably less than the equivalent of this quantity of cyanide, and there is therefore no interference with the quantitative separation of the silver chloride from the decomposition products of the sulphocyanate by filtration of a hot nitric acid solution of 25 per cent. strength.

That small amounts of silver cyanide can be left in the filtrate without interference with the determination of the total silver by means of a sulphocyanate titration might be expected from the fact that in acid solution silver cyanide is much more soluble than silver sulphocyanate. Con-

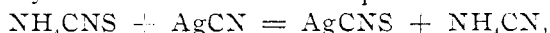
¹ Am. Ch. J., 27, 208 (1902).

² Z. physik. Chem., 26, 264 (1898).

³ Loc. cit.

⁴ Z. anal. Chem., 33, 33 (1894).

sequently the ammonium sulphocyanate added in the titration will decompose the silver cyanide in the sense of the equation :



and it will not be until the ammonium cyanide reaches a considerable concentration that the reverse action will become appreciable. To ascertain how great the concentration of cyanide might safely be allowed to become, the following experiments were conducted ; a silver nitrate solution of about N/15 strength was standardized against an ammonium sulphocyanate solution, and to 15 cc. samples of the silver solution varying quantities of a N/15 potassium cyanide solution were added. In the presence of ferric iron as indicator, sulphocyanate was run into the solution until a strong red color was obtained, the mixture was stirred briskly for five minutes to afford time for the decomposition of the silver cyanide, and then silver nitrate was run in drop by drop, with stirring, to the disappearance of color. One drop more of the sulphocyanate gave in each case a permanent coloration. The quantity of sulphocyanate required for the total silver was then compared with the quantity as calculated from the original standardization of the two solutions. The tabulated results show the variation in cubic centimeters from the true titre of the solutions, the experiment being performed four times for each concentration of potassium cyanide used.

N/15 KCN taken in cc.	Extreme errors, in cc. of N/15 NH ₄ CNS.
0.10	— 0.01 to — 0.04
0.20	— 0.01 to — 0.06
0.30	+ 0.03 to — 0.03
0.40	+ 0.05 to — 0.01
0.50	+ 0.13 to + 0.09
1.00	+ 0.52 to + 0.12

The results show that quantities as great as 0.4 cc. of N/15 potassium cyanide solution do not affect the accuracy of the titration by amounts larger than the errors of measurement, while larger quantities cause perceptible errors in determining the true end-point. In the analytical method proposed, the amount of cyanide left in the solution is much less than half of this maximum amount.

Experiment thus substantiates the correctness of the assumptions involved in our method.

§ 5. Discussion of Existing Methods.

A number of methods have been proposed for the analysis of mixtures of sulphocyanates and chlorides. The time-consuming method of Gondoin¹, depending upon the precipitation and weighing of cuprous sulphocyanate, and that of Alt², depending upon the oxidation of the sulphocyanate to sulphuric acid and its determination as barium sulphate, as

¹ Z. anal. Chem., 36, 528 (1897).

² Ber., 22, 3258 (1889); Z. anal. Chem., 31, 349 (1892).

well as the method of Krug and Ebroy¹, depending upon the solubility of the salts in acetone, were not investigated.

Volhard² proposed a volumetric method depending on the oxidation of the sulphocyanate by standardized potassium permanganate, assuming the correctness of the equation: $\text{NH}_4\text{CNS} + 3\text{O} = \text{NH}_4\text{CN} + \text{SO}_3$. No analytical results accompany the publication of the method, which has nevertheless been incorporated in some text-books. An attempt to use this method resulted in complete failure. Taking a permanganate solution standardized against oxalic acid, and a sulphocyanate solution standardized against silver nitrate, effort was made to compare the two solutions by Volhard's method. The amount of sulphocyanate found varied from 86.2 per cent. to 93.5 per cent. of that actually present, in spite of the fact that conditions of concentration, temperature, and degree of acidity were kept as constant as possible. It was found impossible to obtain either uniformity or correctness of results. This same method has been proposed independently by Jumeau³ and by Alt⁴, the latter stating that the method is inaccurate, but erroneously ascribing the irregularities to the iron usually present in commercial sulphocyanates.

Volhard⁵ also proposed decomposing the sulphocyanate by oxidation with dilute nitric acid at the temperature of the water-bath, then rendering the solution alkaline with ammonium hydroxide, evaporating to drive off the hydrocyanic acid quantitatively, and determining the chloride in the residual solution. Investigation of this method brought to our notice that, although the sulphocyanate is completely decomposed, as Volhard states, yet the subsequent treatment with alkali causes in part the re-formation of the sulphocyanate. This example of a reversible reaction becomes intelligible in the light of Stokes'⁶ proof that a constant decomposition product of sulphocyanic acid is isopersulphocyanic acid, $\text{H}_2\text{N}_2\text{C}_2\text{S}_3$, which reacts with alkaline cyanides according to the equation: $\text{H}_2\text{N}_2\text{C}_2\text{S}_3 + 3\text{KCN} = 3\text{KCNS} + 2\text{HCN}$. In like manner other compounds containing sulphur in the lower stages of oxidation react with cyanides to form sulphocyanates; *e. g.* Gutmann⁷ makes the reaction of thiosulphates with potassium cyanide the basis of a method for the detection of thiosulphates. It is clear therefore that any method for the analysis of the mixtures under discussion will be faulty if the solution is rendered alkaline before complete oxidation of the sulphur, which opera-

¹ J. Anal. Appl. Chem., 6, 184.

² Ann., 190, 1 (1878); Z. anal. Chem., 18, 291 (1879).

³ Bull. soc. chim., [3] 9, 346 (1893).

⁴ Loc. cit.

⁵ Z. anal. Chem., 18, 282, (1879).

⁶ This Journal, 29, 446 (1907).

⁷ Z. Nahr.-Genussm., 13, 261; Chem. Zentr., 1907, I, 1152; Chem. Abstracts, 1907,

tion was found by Treadwell¹ to require two hours when the oxidizing agent was fuming nitric acid.

Borchers² proposes the precipitation of chloride and sulphocyanate as their silver salts, and the determination of their sum by Volhard's method: the precipitate is then washed into a flask with a stream of concentrated nitric acid and boiled with that reagent for three-quarters of an hour to the complete decomposition of the silver sulphocyanate; the solution is diluted and filtered, and the silver determined in the filtrate. Experience showed that the long boiling with concentrated nitric acid renders the method entirely unsuited for ordinary laboratory use.

Barnes and Liddell³ precipitate the sulphocyanate as its cuprous salt by titration with copper sulphate in the presence of a bisulphite, the end-point of the reaction being determined by a drop test with potassium ferrocyanide. The authors note that the end-point cannot be determined exactly owing, as they state, to the oxidation of the copper in the cuprous sulphocyanate and its reaction with the ferrocyanide. We were unable to devise any method for rendering the determination of the end-point more exact, and found the method of use only for approximating the correct values.

Diehl⁴ also precipitates the sulphocyanate as its cuprous salt, using excess of copper sulphate and a bisulphite, filters off the precipitate, and determines the chloride in the filtrate. Noyes and Abbot⁵ investigated this method, and found variations between + 0.27 per cent. and - 0.49 per cent. in the amount of chlorides found; the method can therefore not be regarded as exact. Mann⁶ has proposed a substitution of hydrogen sulphide for the bisulphite as a reducing agent; his results for the chloride vary from the true figures by -0.3 per cent. to - 2.8 per cent.

Incidentally to a physico-chemical research, Knüpferr⁷ proposed the oxidation of the sulphocyanate by acid potassium iodate. After boiling off the hydrocyanic acid, or cyanogen, as he believes it to be, he reduces the excess iodate with sulphur dioxide, oxidizes with a nitrite and boils again to expel the iodine completely; the chloride is determined in the residue. The figures given indicate that the method is accurate; it is made very tedious, however, by the repeated boilings necessary for quantitative expulsion of the hydrocyanic acid and the iodine.

¹ *Analytical Chem.*, Vol. II, p. 261. (New York, 1906).

² *Z. anal. Chem.*, **22**, 92 (1883); Borchers' *Repert. anal. Chem.*, **1881**, 130; Treadwell's *Anal. Chem.* II, p. 261.

³ *J. Soc. Chem. Ind.*, **2**, 122 (1883).

⁴ *Chem. Zentr.*, **1883**, 649; *Ber.*, **16**, 2319 (1883).

⁵ *Z. physik. Chem.*, **16**, 129 (1895).

⁶ *Z. anal. Chem.*, **28**, 668 (1889).

⁷ *Z. physik. Chem.*, **26**, 262 (1898).

The method of Rupp and Schied¹, depending upon the oxidation of the sulphocyanate by free iodine in bicarbonate solution and titration of the unused iodine, was shown by Thiele² to be inaccurate, owing to the incomplete oxidation of the sulphocyanate in the half-hour's time proposed by Rupp and Schied. Thiele states that if the oxidation be continued for four hours the results are accurate; in this modified form Rupp³ has adopted the method, and claims good results from its use. In view however of Stokes' results on the decomposition of sulphocyanates and Treadwell's statement that complete oxidation to sulphuric acid requires the most vigorous treatment with fuming nitric acid, it may be doubted whether the oxidation by iodine follows quantitatively the simple equation expressed.

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THE USE OF SODIUM CARBONATE AND ZINC OXIDE IN SULPHUR AND ARSENIC DETERMINATIONS.

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A method involving the use of sodium carbonate and zinc oxide for sulphur and arsenic determinations was devised by one of us⁴ some years ago, and has given uniform satisfaction in various assay offices for so long a time that an account of it should be made public.

One part of dry sodium carbonate and four parts of zinc oxide are mixed thoroughly. In the case of sulphur determinations a weighed sample of the material to be analyzed, usually one half gram, is mixed intimately with enough of the sodium carbonate-zinc oxide reagent to afford at least twice as much sodium carbonate as would be required by the sulphur, arsenic, etc., present, placed in a small porcelain dish, covered with the reagent and heated to redness in a muffle for fifteen or twenty minutes. A shorter period of heating is usually sufficient, but the time here specified is ample for all cases. The residue is then extracted with water, boiled, filtered, the filtrate made acid with hydrochloric acid, precipitated with barium chloride, and the barium sulphate treated as usual.

In an arsenic determination the substance is treated as above until the alkaline solution is filtered from the residue. This filtrate is acidified with acetic acid, precipitated with silver nitrate, boiled for a few minutes and then filtered. The precipitate of silver arsenate is washed thoroughly with hot water and then dissolved in dilute nitric acid, its silver content being determined finally by titration with ammonium or potassium sul-

¹ Ber., 35, 2191 (1902).

² Ber., 35, 2766 (1902).

³ Arch. Pharm., 243, 468 (1905); This Journal, 28, 1771 (1906); J. Chem. Soc. (Abstracts) 88, 867 (1905).

⁴ C. B. S.