

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF THE UNIVERSITY OF NEBRASKA]

THE USE OF BUFFERED AMMONIA IN THE IODIMETRIC THIOCYANATE DETERMINATION

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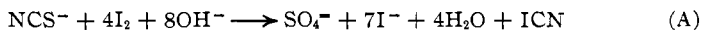
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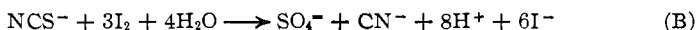
The suitability of borax as a non-volatile alkaline buffer to accelerate the oxidation of thiocyanate with iodine was shown by Pagel and Ames.¹ A. Schwicker² used a solution of ammonium borate as buffer (synthetically prepared by adding approximately the equivalent amount of boric acid to ammonia). Both methods give accurate results.

In case, however, it is desired to determine borate in the same sample, both of the above methods would be undesirable. Schwicker suggests that dilute ammonia accelerates the oxidation, but that there is danger of the formation of insoluble iodides of nitrogen unless the ammonia is added with extreme care; hence he discourages its use.

We have found, however, that the proper amount of dilute ammonia containing about an equivalent amount of ammonium salt does not react irreversibly with iodine, even with a large excess of iodine on long standing. Furthermore, a fixed volume of this solution gives accurate results independent of a wide range of volume and of thiocyanate (Table III). From the oxidation reaction in alkaline medium



it is apparent that equivalent amounts of hydroxyl and iodine are required. Upon acidification the iodocyanogen again reacts with iodide, liberating free iodine; hence the net reaction used as a basis of computation is



With this in view an amount of ammonia was chosen which should contain sufficient reserve hydroxyl to provide for the oxidation of a large amount of thiocyanate, and still not be too alkaline in case only small amounts of thiocyanate were present. Thus, for instance, 20 cc. of 1 *N* ammonia should provide for 150 cc. of titration with 0.1 *N* iodine and still leave in excess 5 cc. of 1 *N* ammonia to insure complete oxidation. It should also be noted that large amounts of additional ammonium salts do not interfere with either the accuracy or the time required for complete oxidation.

Materials and Apparatus.—The preparation of solutions and type of apparatus used in this work was in general identically as described in a previous publication.¹ The additional reagents used were all "Highest Purity;" nevertheless blanks were run in all cases to detect traces of thiocyanate or other interfering impurities.

¹ Pagel and Ames, *THIS JOURNAL*, **52**, 2698, 3093 (1930).

² A. Schwicker, *Z. anal. Chem.*, **77**, 278 (1929).

Experimental

Various amounts of ammonium sulfate (ranging from 1 to 6 g.) were dissolved in 20 cc. of 1 *N* ammonia and the resulting solution diluted with water to 150 cc. Then 25 cc. of 0.1 *N* iodine was added and the mixture allowed to stand from five to fifteen minutes in a dark cupboard. After acidifying with 5 cc. of 6 *N* hydrochloric acid, the iodine was immediately titrated slowly with thiosulfate, using starch indicator after the iodine color had been almost completely discharged. The equivalent amounts of iodine were also prepared from pipetted portions of standard iodate and 3 g. of potassium iodide, treated with a slight excess over the calculated amount of hydrochloric acid. The buffered ammonia solution was then added to the liberated iodine and the procedure completed as above. In both cases the thiosulfate titrations agreed identically with values obtained in the iodine-thiosulfate ratios determined in the usual manner. Ammonium chloride and nitrate substituted for the sulfate likewise gave perfect results. The analyses of known amounts of thiocyanate (tabulated in Tables I, II and III) were carried out according to the method given in the procedure below.

Procedure

The solution containing the thiocyanate in a volume of 150 to 300 cc. should be practically neutral to litmus. Any excess of strong acid or base should be neutralized. Slight acidity or alkalinity due to hydrolysis of salts may be ignored. If heavy metals which produce insoluble hydroxides are present, ammonia is added until faintly alkaline to litmus. The buffer solution containing 1 g. of ammonium salt (sulfate, chloride or nitrate) dissolved in 20 cc. of 1 *N* ammonia is then added and the mixture treated with standard iodine with a minimum excess of 5 cc. This excess is determined with sufficient accuracy by comparing colors with 5 cc. of iodine in a similar volume of water. (This reference solution should be prepared before starting the titration.) A larger excess of iodine does no harm. After standing for four to five minutes the solution is acidified with an excess of about 5 cc. of 6 *N* hydrochloric acid and the excess iodine immediately titrated with standard thiosulfate.

In case standard iodate is used as a source of iodine, certain modifications may be necessary. If the salts of heavy metals or of weak acids are absent, the iodate and potassium iodide may be added directly to the neutral solution of thiocyanate. A small excess of hydrochloric acid (1 or 2 cc. of 1 *N*) in addition to the calculated amount is then added. (A large excess of acid must be avoided since this would unnecessarily neutralize large amounts of the ammonia buffer.) The ammonia buffer solution is then added, the mixture allowed to stand for four to five minutes and the determination completed as stated above.

In case heavy metals or salts of weak acids are present, the iodine must be liberated in a separate flask, and the faintly alkaline mixture containing the thiocyanate is added to the liberated iodine. The ammonia buffer may be added either to the liberated iodine or the faintly alkaline thiocyanate mixture.

Table I shows the results obtained using standard iodine, with 20 cc. of 1 *N* ammonia and 6 g. of the given ammonium salt as buffer. The volume during oxidation was approximately 150 cc. Five minutes was allowed for complete oxidation. Identical results were obtained in fifteen minutes. The excess iodine to that required for reaction (A) ranged from approximately 5.3 to 6.5 cc. (namely, the difference between "iodine added" and $\frac{4}{3}$ times "calcd. iodine").

TABLE I
RESULTS USING STANDARD IODINE

0.07278 <i>N</i> KSCN, cc.	Buffer salt	G.	Iodine, 0.0998 <i>N</i>			Error, %
			Added, cc.	Reduced, cc.	Calcd., cc.	
50	(NH ₄) ₂ SO ₄	6	55.00	36.38	36.46	-0.2
50	(NH ₄)Cl	6	55.00	36.40	36.46	-.2
50	(NH ₄)Cl	6	55.00	36.37	36.46	-.2
25	(NH ₄) ₂ SO ₄	6	30.00	18.20	18.23	-.2
25	(NH ₄) ₂ SO ₄	6	30.00	18.21	18.23	-.1
25	(NH ₄)Cl	6	30.00	18.22	18.23	.0
25	(NH ₄)Cl	6	30.00	18.20	18.23	-.2
10	(NH ₄)Cl	6	15.00	7.28	7.29	-.1
10	(NH ₄)Cl	6	15.00	7.28	7.29	-.1

Table II shows that accurate results are obtained in large or small oxidation volumes, using iodate as a source of iodine with 1 g. of ammonium salt.

TABLE II
RESULTS USING STANDARD IODATE

0.07278 <i>N</i> KSCN, cc.	Vol., cc.	Buffer salt	Iodate, 0.1000 <i>N</i>			Error, %
			Added, cc.	Reduced, cc.	Calcd., cc.	
50	150	(NH ₄) ₂ SO ₄	55.00	36.36	36.39	-0.1
50	150	(NH ₄) ₂ SO ₄	55.00	36.38	36.39	.0
50	350	(NH ₄) ₂ SO ₄	55.00	36.34	36.39	-.1
50	150	NH ₄ Cl	55.00	36.34	36.39	-.1
50	350	NH ₄ Cl	55.00	36.33	36.39	-.2
25	350	(NH ₄) ₂ SO ₄	30.00	18.15	18.19	-.2
25	350	(NH ₄) ₂ SO ₄	50.00	18.18	18.19	-.1
25	150	NH ₄ Cl	30.00	18.15	18.19	-.2
25	350	NH ₄ Cl	30.00	18.15	18.19	-.2
25	150	NH ₄ NO ₃	30.00	18.15	18.19	-.2
25	350	NH ₄ NO ₃	30.00	18.14	18.19	-.3
10	150	(NH ₄) ₂ SO ₄	15.00	7.26	7.28	-.3
10	350	NH ₄ Cl	15.00	7.25	7.28	-.4

As previously stated, Table III shows that 20 cc. of 1 *N* ammonia even in the presence of large amounts of ammonium salt provides for large

amounts of thiocyanate. Borax does not interfere; furthermore, large amounts of precipitated hydroxides have no effect on the completeness of oxidation. In a series of comparable determinations (not shown), it was found that the oxidation was apparently complete in two minutes, but four to five minutes is recommended in all cases.

In Table III, 20 cc. 1 *N* ammonia containing 1 g. of ammonium sulfate was used as buffer. The additional salts added are listed.

TABLE III
EFFECT OF SALTS ADDED

0.07278 <i>N</i> KSCN, cc.	Vol., cc.	Salts added G.	Salt	Iodate, 0.1000 <i>N</i>			Error, %
				Added, cc.	Reduced, cc.	Calcd., cc.	
100	250	5	(NH ₄) ₂ SO ₄	105.00	72.72	72.78	-0.1
100	250	5	(NH ₄) ₂ SO ₄	105.00	72.71	72.78	-.1
50	150	5	(NH ₄) ₂ SO ₄	60.00	36.37	36.39	-.1
50	350	5	(NH ₄) ₂ SO ₄	55.00	36.32	36.39	-.2
25	350	9	(NH ₄) ₂ SO ₄	30.00	18.13	18.19	-.3
25	350	9	(NH ₄) ₂ SO ₄	30.00	18.11	18.19	-.4
25	350	2	NaNO ₃	50.00	18.17	18.19	-.1
25	350	2	NaNO ₃	50.00	18.18	18.19	.0
10	350	5	(NH ₄) ₂ SO ₄	15.00	7.29	7.28	+ .1
10	350	5	(NH ₄) ₂ SO ₄	15.00	7.28	7.28	.0
25	200	2	ZnSO ₄ ·7H ₂ O	50.00	18.15	18.19	-.2
25	200	2	ZnSO ₄ ·7H ₂ O	30.00	18.13	18.19	-.3
25	200	2	MgCl ₂ ·6H ₂ O	30.00	18.15	18.19	-.2
25	200	4	Al ₂ (SO ₄) ₃ ·18H ₂ O	30.00	18.16	18.19	-.2
25	250	3	Na ₂ B ₄ O ₇ ·10H ₂ O	30.00	18.17	18.19	-.1
25	250	3	Na ₂ B ₄ O ₇ ·10H ₂ O	30.00	18.14	18.19	-.3
25	250	3	NaC ₂ H ₃ O ₂ ·3H ₂ O	50.00	18.14	18.19	-.3

Nickel, cobalt and manganese, even in relatively small amounts, produced very erratic results.

Summary

It has been shown that the proper amount of ammonia treated with ammonium salts gives the proper alkalinity for the rapid iodimetric determination of thiocyanate, over a wide range of conditions.

Data, and the details of procedure, and also a citation of some interfering metallic radicals, have been included.

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