P_2O_5 was found. When the precipitation for the same amounts had stood 17 hours, however, there was apparently 0.0145 gram P_2O_5 . From these experiments it appears that with the small amounts of vanadium and phosphorus occurring in soils, a satisfactory separation can be made with magnesia mixture provided the precipitate does not stand more than 3-4 hours. No experiments have been carried out on larger amounts.

THE NATURE OF THE MIXED YELLOW PRECIPITATE

It was first assumed that vanadium replaced the phosphorus in the yellow precipitate. Later consideration showed, however, that this was unlikely, for the precipitation of vanadium is complete¹ when phosphoric acid in amounts somewhat less than ten times the amount of vanadic acid is present, and Brearley and Ibbotson have shown that the results obtained by weighing the yellow precipitate are low when vanadium is present. To test this point mixtures of phosphoric and vanadic acids were precipitated under conditions outlined in *Bull.* 107 (revised) of the Bureau of Chemistry of this Department, and titrated with standard alkali. The results are given in Table V below.

TABLE V—SHOWING THE ACIDITY OF THE PHOSPHOMOLYBDATE PRECIPITATE OBTAINED IN THE PRESENCE OF VANADIUM

No.	1	2	3	4
Grams P_2O_5 present.....	0.00432	0.00432	0.00432	0.00432
Grams V_2O_5 present.....	None	0.00125	0.00250	0.00500
Grams P_2O_5 found.....	0.00432	0.00396	0.00337	0.00298

The latter determinations showed incomplete precipitation. The precipitation was made complete and the phosphorus coming down was estimated gravimetrically. The amount of phosphoric acid recovered was added to that found by titration, making the final figures for Experiments 2, 3 and 4: 0.0045, 0.0045 and 0.0042, respectively. It thus appears that the acidity of the yellow precipitate is not increased by the presence of vanadium and that volumetric determinations of phosphorus in presence of vanadium are apt to be low. Apparently the vanadium replaces the molybdenum instead of the phosphorus as indicated by Blum.²

COMPOSITION OF THE FEATHERY PRECIPITATE

When the phosphomolybdate precipitate is dissolved in ammonia there is sometimes a white precipitate resembling ferric phosphate which fails to dissolve. Hillebrand³ states that this is a compound of phosphorus and recommends the addition of a small amount of citric acid or in case this fails to dissolve it, fusion with sodium carbonate. Hornberger⁴ finds this precipitate contains titanium and phosphorus. It may be ferric, titanium or aluminum phosphates and hydroxides or mixtures of these, depending on the composition of the solution. It is a combination of phosphorus with the above bases that have been absorbed or not thoroughly washed away. If the solution is made sufficiently acid before the precipitation and nearly neutral ammonium molybdate added with stirring, one need not fear the formation of this precipitate

unless the concentration of phosphoric acid and bases is large. In such cases a second precipitation is the most expedient procedure.

One gram of soil from the Hawaiian Islands, containing 4.95 grams P_2O_5 and large amounts of iron, aluminum and titanium, was precipitated in small volume without much stirring and the residue insoluble in ammonia set aside and analyzed. It contained 0.0017 Al_2O_3 , 0.0058 TiO_2 and 0.0016 Fe_2O_3 , combined with phosphorus. Two precipitations on the same amount conducted in a like manner yielded a precipitate containing 0.0004 TiO_2 , 0.0001 Fe_2O_3 , no Al_2O_3 and an almost negligible amount of phosphorus. The precipitate obtained from some American soils contained only a trace of titanium and was largely aluminum.

The feathery precipitate deliberately obtained in small amounts from eight samples of soil weighed from 0.0004 to 0.0008 gram. In three cases only did the precipitate of $Mg_2P_2O_7$ obtained from the above precipitates exceed the blank determination and these by 0.0001 gram only.

When precipitation of the phosphomolybdate is carried on in such a manner that it does not adhere to the sides of the beaker or flask and washing is thorough, the feathery precipitate can easily be avoided in soil determinations.

CONCLUSIONS

I—The fusion methods, Washington's method and Fischer's method, of treating the soil for the determinations of phosphorus, give accurate results.

II—Vanadium interferes with the phosphorus determinations in soils. This influence can be avoided by reducing the vanadium with ferrous sulfate and precipitating at low temperatures by shaking. With soil solutions it is not necessary to add sulfurous acid to prevent the reoxidation of the vanadyl salt. The influence of vanadium is also avoided by using the gravimetric method, provided precautions are taken for complete precipitation and the ammonium magnesium phosphate precipitate is not allowed to stand too long.

III—Tungsten and titanium do not interfere with the determination of phosphorus in soils, by the gravimetric method, provided precautions are taken to make the precipitation complete.

IV—The composition of the feathery precipitate is dependent on the nature of the bases in the solution before precipitation. Proper precipitation and washing of the yellow precipitate prevents the formation of the feathery precipitate or reduces it to a negligible amount.

BUREAU OF SOILS, WASHINGTON, D. C.

SOME NEW METHODS FOR THE ANALYSIS OF LIME-SULFUR SOLUTIONS¹

By ROBERT M. CHAPIN

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INTRODUCTORY

The important substances contained in lime-sulfur solutions are calcium polysulfides and calcium thio-

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¹ Cain and Hostetter, *Loc. cit.*

² *J. Am. Chem. Soc.*, **30** (1908), 1858.

³ U. S. Geol. Survey, *Bull.* **422** (1910), 145.

⁴ *Landw. Vers. Sta.*, **82** (1913), 299.

sulfate. In addition, theoretically at least, the solutions may be either basic through the presence of free calcium hydroxide, calcium hydroxysulfide, etc., or acidic (regarding hydrogen sulfide as an "acid") through the presence of free hydrogen sulfide, calcium hydrosulfide, etc. Dilute solutions of sulfides of calcium are notably hydrolyzed, and since both base and acids are diatomic, the possible molecules and ions are numerous and complex. The writer takes the position that analytical figures¹ inherently dependent upon or modified by degree of dilution can be of little value since such figures can afford no fixed basis for comparison between manufactured products of unequal degrees of concentration, and are still less applicable to the diluted solutions used in practice. The important problem in this connection is to determine the balance between the positive and the negative constituents; that is, to ascertain quantitatively whether a solution contains excess lime or excess hydrogen sulfide. The present paper describes methods for determining the concentration of total (sulfide) base, of total (sulfide) acid and of excess base or acid.

DESCRIPTION OF METHODS

The methods are all titration methods, performed with $N/10$ solutions upon 10 cc. of lime-sulfur solution.² Moreover, they all ultimately measure either CaA_2 or M_2S_x . Therefore the figures of the titrations are directly comparable and for the purpose of the present study the results are best given in that form without calculating to percentages of the actual substances present. The determinations are designated and defined as follows:

I—SULFIDE-BASE FIGURE, representing cc. of $N/10$ base present in 10 cc. of solution, whether existing as "free lime" or as various possible calcium sulfides.

II—REACTION FIGURE, representing cc. of $N/10$ base or acid (hydrogen sulfide) present in 10 cc. of solution *in excess* of the quantity necessary to form neutral salts of the formula CaS_x . If the solution contains an excess of base the reaction figure carries a plus sign; if an excess of acid, a minus sign..

III—SULFIDE-ACID FIGURE, representing cc. of $N/10$ acid (H_2S_x) present in 10 cc. of solution, whether existing free or as various possible calcium sulfides.

Lime-sulfur solutions are affected by exposure to air. Hence a sample is best preserved³ by distribution among small, wholly filled and well sealed bottles, kept in a dark, cool place. The solution is to be clarified by sedimentation, never by filtration. A clean, dry pipette must be used for measuring each portion, for the skin of solution adhering to the walls of a pipette after drainage may undergo sufficient change to in-

fluence appreciably the composition of another charge immediately drawn into it. Lastly, the charge should always be delivered from the pipette into an appropriate liquid previously placed in the container in which the titration is to be executed, keeping the tip of the pipette constantly just under the surface of the liquid until necessary to raise it for drainage at the end.

DISCUSSION AND EXECUTION OF METHODS

I. SULFIDE-BASE FIGURE—The method employed is the obvious one, well described by Tartar and Bradley,¹ of titration with standard acid in presence of an appropriate indicator not sensitive to hydrogen sulfide. Into a 100 cc. Erlenmeyer flask containing 30 cc. water, is pipetted 10 cc. of the sample. The liquid is slowly titrated with $N/10$ hydrochloric acid until the yellow tint has gone, then one drop of methyl orange is added and the titration continued to a clear end-point. In a duplicate the addition of methyl orange is delayed as long as possible, to avoid bleaching or adsorption of the indicator—with a slight orange tint—by freshly precipitated sulfur. Instead of the methyl orange recommended by Tartar and Bradley, congo-red, recommended by Ramsay,² may be employed and may be preferred by some. It should be added similarly just before the end of the titration and just enough (it is necessary to dilute the ordinary indicator solution) is to be used to produce a distinct scarlet. As the titration progresses the scarlet becomes less intense, merely through coagulation of the sulfur in the background, but the purity of the tint remains until the end, where distinct modification occurs.

If the sample is a bath much used for dipping cattle or sheep both methyl orange and congo-red fail, but another indicator, sodium nitroprusside, appears reliable even in very dirty solutions. In a general way it has long been known that sodium nitroprusside, in the presence of hydrogen sulfide, is an indicator of neutrality, but the writer is unaware of its previous practical application in alkalimetry. Into 30 cc. of water in a 100 cc. beaker is pipetted 10 cc. of the sample, and the liquid is slowly titrated with $N/10$ hydrochloric acid until the yellow color, which in case of used dipping baths may partly be due to extraneous matter, has become faint. A drop of the liquid is transferred to a white spot plate and treated with one drop of a 0.2 per cent solution of sodium nitroprusside, recently prepared and kept in an amber bottle. If the titration is still far from complete the well known violet will quickly develop and soon fade. If the color is doubtful or does not appear, enough of the well stirred liquid to nearly fill one of the cups of the spot plate is transferred thereto with a medicine dropper and immediately treated with one drop of the indicator solution. The medicine dropper is conveniently kept in a small beaker of distilled water, which serves to rinse it between tests. The end of the titration is indicated by the failure of a dirty green turbidity (in no way resembling the former clear violet) to appear within fifteen minutes

¹ Compare certain methods of Thompson and Whittier, *Del. Coll. Agric. Exper. Sta. Bull.* 105, June 1, 1914.

² The writer's concern with lime-sulfur solutions is confined to those used for dipping cattle and sheep under official regulations (B. A. I. Order 210 and Amendments). The regulations set standards of strength of 2 per cent and 1.5 per cent of "sulfide sulfur." Accordingly, the methods are adjusted for convenient work on samples from the field—which are often small—of such approximate strength. Increasing the quantity of sample and using stronger solutions for titration might very likely improve accuracy in some of the methods.

³ The writer has previously noted (*Dept. Bull.* 163) that samples of dipping baths through which cattle and sheep have passed in large numbers are subject to deterioration even when sealed from air.

¹ *THIS JOURNAL*, 2 (1910), 271.

² *Journal of Agricultural Science*, 6 (1914), 476.

of quiet standing in diffused daylight. It is naturally best to make a preliminary coarse titration, and then, by subsequent repetitions, to narrow the location of the end-point to the desired degree of definiteness. In such subsequent titrations not more than three tests should be made during any one, and these tests should be carried through without any intermediate delays to see whether color is going to develop or not. The writer will not now undertake any discussion of the rationale of the color production¹ or of its application to anything but the titration of lime-sulfur solutions. Here he has found the titration precise, the end-point sharp to less than 0.10 cc. of *N*/10 acid, and consistent with the end-points yielded by the other two indicators. Indeed, working to 0.1 cc. on pure solutions, it is easier to be positively assured of the attainment of the end-point when using sodium nitroprusside than when using either methyl orange or congo-red, though its application is so tedious that the two latter indicators will be preferred where practicable.

II. REACTION FIGURE—Some years ago Harris² proposed to determine "monosulfide sulfur" by simple titration with *N*/10 iodine until the original yellow color just disappears. He bases the validity of his method on the supposition that "the reaction

goes to completion before the reaction between the iodine and calcium thiosulfate commences." In view of the considerable investigation by different chemists to which Harris' work has been subjected, it is surprising that no one has yet noted the obvious fallacy upon which the method is based. For, passing over the truth of Harris' unproven assumption of a selective action whereby iodine reacts more readily with calcium polysulfide than with calcium thiosulfate, it ought to be plain enough that such a selective action can lead to quantitative results only when complete admixture is made instantaneously. During actual titration, especially toward the end, when the concentration of calcium polysulfide has become relatively small, the iodine solution, as it drops from the burette, must be regionally in great excess as respects calcium polysulfide and must then necessarily react with any contiguous molecules of calcium thiosulfate.

The only possible way in which Harris' method can afford uniformly dependable results is through the assumption of the reaction represented by the equation $\text{CaS}_x + \text{CaS}_4\text{O}_6 = 2\text{CaS}_2\text{O}_3 + \text{S}_x$, whereby any tetrathionate formed by the action of iodine upon thiosulfate is at once decomposed by polysulfide and the original amount of thiosulfate regenerated. As a matter of fact this reaction has been known for many years and is noted in the larger treatises. But the conditions under which Harris' method are executed are such that the above noted reaction does not always progress normally, and for this and other reasons³ the method cannot be regarded as trustworthy.

¹ The phenomenon is possibly dependent upon the presence of thiosulfate (cf. Casolari, *Rend. soc. chim. ital.*, [2] 5 (1914), 294; *C. A.*, 9 (1915), 1435.

² *Mich. Agric. Coll. Exper. Sta. Tech. Bull.*, 6, Jan., 1911.

³ Compare McDonnell, *Bur. Chem. Bull.* 162, p. 38, Nov., 1913.

Considering now the equation

it is evident that one result of the reaction is to exchange for the weak and volatile acid, hydrogen sulfide, an equivalent amount of relatively strong thiosulfuric acid. Consequently if a strictly neutral solution of sodium tetrathionate be added in excess to a lime-sulfur solution, the resulting liquid becomes titratable with use of the ordinary indicators appropriate for moderately strong acids. The resultant figure for acidity or alkalinity must be the figure for acidity or alkalinity of the original lime-sulfur solution.

Preliminary investigation revealed that the reaction progresses normally only in alkaline solutions, not in presence of free hydrogen sulfide. On the other hand, alkalis decompose solutions of tetrathionates with production of acidity and iodine-absorbing power. The dilemma was avoided by rendering the solution alkaline to a small degree with ammonia only. Under such properly adjusted conditions, which are easily produced, the reaction progresses rapidly and normally without the occurrence of appreciable decomposition of excess tetrathionate.

Since the tetrathionate solution undergoes slow decomposition in any event, it should be prepared only in the quantity and at the time needed. Into a 250 cc. conical flask bring an excess (ordinarily about 25 per cent more than the titration for "sulfide-base figure") of *N*/10 iodine and mix in *N*/10 sodium thiosulfate until the color is nearly discharged. Add a little *N*/10 hydrochloric acid to destroy any iodate, rinse down the sides of the flask and cautiously titrate with *N*/10 thiosulfate against a white background till the yellow tint just vanishes. Add 5 cc. of 10 per cent ammonium chloride, dilute to 100 cc., add one drop methyl red indicator solution (0.2 per cent methyl red in alcohol), titrate with *N*/10 caustic soda to alkalinity, then carefully bring back to a distinct orange with *N*/10 hydrochloric acid; pipette in, while mixing, 10 cc. of *N*/10 caustic soda. Now pipette in 10 cc. of the sample, mix well, and let stand three minutes, preferably stoppering the flask. Then add one drop more of methyl red, and titrate with *N*/10 acid to a distinct end-point. Determine the equivalence of 10 cc. of the *N*/10 alkali in terms of the *N*/10 acid and algebraically subtract it from the actual titration to obtain the "reaction figure." In duplicating the determination the amount of *N*/10 caustic soda should be adjusted—in multiples of 5 cc.—so that back titration with *N*/10 hydrochloric acid will require between 5 cc. and 10 cc. All the operations are to be carried through without intermediate delays.

III. SULFIDE-ACID FIGURE: METHOD A—Algebraically subtract the "reaction figure" from the "sulfide-base figure."

METHOD B—The liquid resulting from the determination of the "reaction figure" contains, in addition to the original thiosulfate of the sample, newly formed thiosulfate in amount exactly equivalent to the

M_2S_x originally present in the sample. Therefore, after addition of starch the liquid is titrated with $N/10$ iodine. From the resulting total iodine titration must be subtracted the thiosulfate titration,¹ in order to obtain the desired result.

METHOD C—Methods A and B, though preferable on the score of accuracy where they can be applied, fail on used dipping baths. For such baths Method C is the recourse, while in any case it affords a simpler and more direct road to the desired information. The method consists simply in titrating an ammoniacal dilution of the sample with standard tetrathionate, until an appropriate indicator no longer shows a trace of sulfide remaining.

To prepare the standard $N/20$ tetrathionate, place a convenient quantity of $N/10$ iodine in a dry capacious flask, and mix in $N/10$ thiosulfate until the color of iodine becomes faint, then carefully finish from a burette until the yellow tint vanishes. If the normality of the iodine is a and the normality of the thiosulfate b , then, disregarding insignificant changes in molecular volumes, the normality of the tetrathionate is $\frac{a b}{a + b}$, or, if the two original solutions do

not differ in strength from each other and from true $N/10$ by more than 5 per cent, the normality factor $\frac{a + b}{4}$ is sufficiently close. The tetrathionate solution, being subject to slow decomposition, should be prepared not long before use, especially since it is so easily duplicated at any time from the original solutions.

Into 10 cc. of dilute ammonia (10 volume per cent of concentrated ammonia water) is pipetted 10 cc. of the lime-sulfur solution and the liquid, under constant stirring, is titrated with standard tetrathionate until the yellow tint disappears, or in case of used dipping baths, becomes faint. For finishing the titration a one per cent solution of nickel sulfate is used as an indicator, with a white spot plate and a medicine dropper, as in obtaining the end-point of the sulfide-base titration with sodium nitroprusside. But in this case it is better to place a drop of the nickel sulfate on the plate first, then to add enough of the solution under titration to fill the cup if color does not appear with the first drop. The end-point, passing from faint gray to faint bluish green, is much sharper than any the writer has been able to obtain with any indicator when a metallic salt solution is used as the titrating agent, largely because of the relatively small bulk of the precipitated sulfur compared with that of insoluble metallic sulfides. It is recommended, however, not to attempt to catch the end-point closer than within limits of 0.2 cc. of $N/20$ tetrathionate. If two tests, 0.2 cc. apart, are respectively positive and negative, the true end-point may fairly be taken at the intermediate 0.1 cc. To this figure is then to be added a correction for the end-point of 0.2 cc. $N/20$

¹ Method given in *Bur. Chem. Bull.*, 152 (1912), 70. In view of the usually small titration the writer always adds about 1 g. potassium iodide to the solution before titration to insure proper development of the end-point.

tetrathionate. The fewer the tests and the less the time consumed in titration, the more accurate will naturally be the result. A 0.2 per cent solution of sodium nitroprusside, as an indicator, affords a more conspicuous color until just before the end-point and so may be useful in titrating very dirty solutions. But just at the end-point it is not quite so sensitive as nickel sulfate and yields a very evanescent color. Its use demands a slightly higher correction for end-point, probably 0.4 cc. of $N/20$ tetrathionate.

EXPERIMENTAL

I. COMPARISON OF INDICATORS FOR SULFIDE-BASE DETERMINATION—The personal factor involved in the use of indicators limits the value of experimental results, but since a new indicator is here proposed it is necessary to give some evidence of its probable reliability. The samples were prepared by diluting highly concentrated proprietary preparations. The pairs of figures for nitroprusside indicator show the limits within which the end-point was located in each titration.

TABLE I—COMPARISON OF INDICATORS FOR SULFIDE-BASE TITRATION
Results expressed in cc. $N/10$ HCl per 10 cc. sample

Sample	Methyl orange	Congo-red	Sodium nitroprusside
A.....	21.60	21.55	21.50-22.00
		21.55	21.60-21.80
	21.62	21.45	21.50-21.60
	Av., 21.61	Av., 21.52	Av., 21.60
B.....	20.70	20.64	20.50-20.70
	20.63	20.64	20.60-20.70
	Av., 20.67	Av., 20.69	20.70-20.80
		Av., 20.66	20.60-20.70
			Av., 20.68

The spot plate must be left at rest full fifteen minutes before a final decision is made. On long standing the positive tests tend to fade to a brownish tint, while the negative tests take on a transparent greenish tint, but these changes in no respect affect the sharp location of the end-point. For plain sodium sulfide solutions the nitroprusside indicator is not so satisfactory.

2. DECOMPOSITION OF TETRATHIONATE IN ALKALINE SOLUTIONS—A tetrathionate solution was prepared by nearly decolorizing $N/10$ iodine with $N/10$ thiosulfate, then adding a little hydrochloric acid to decompose any iodate, and finishing by titrating with thiosulfate from a burette, without starch. The solution was then made faintly orange to methyl red. Portions of 75 cc. of the neutralized tetrathionate

TABLE II—THE DECOMPOSITION OF TETRATHIONATE IN ALKALINE SOLUTIONS

Test No.	Temperature of Solution, 28° C.				
	Cc. of 10 per cent NH_4Cl added	Cc. $N/10$ NaOH added	Time of standing Minutes	Cc. $N/10$ HCl for titration	$N/10$ I for titration
1	0	10	10	1.13	7.52 cc.
2	5	10	10	9.97	1.5 drops
3	5	10	20	9.92	2 drops
4	5	10	40	9.90	3 drops
5	0	0	200	0	1 drop

solution were brought into 300 cc. glass-stoppered Erlenmeyer flasks and made to 100 cc. with or without the addition of ammonium chloride: $N/10$ caustic soda was then pipetted in with thorough mixing, the flasks were stoppered and left standing definite periods. Finally the solutions were titrated, first with $N/10$ hydrochloric acid and methyl red, then

with $N/10$ iodine and starch. The hydrochloric acid was standardized in a parallel manner, by titrating against 10 cc. of the $N/10$ caustic soda in 100 cc. distilled water.

In the iodine titration of test No. 2 one drop of iodine yielded a very faint blue, but too faint to be comparable to an ordinary titration. The results indicate that in a regular determination, carried through according to directions, the error due to decomposition of tetrathionate can scarcely amount to more than one drop of either $N/10$ hydrochloric acid or iodine.

3. TESTS OF METHODS I, II, IIIA AND IIIB ON LIME-SULFUR SOLUTIONS—An approximately double-strength dilution, prepared from a commercial concentrated lime-sulfur solution, was distributed among small bottles, well filled and sealed. Measured portions of this stock solution were then diluted with equal parts of water, $N/20$ caustic soda, and $N/20$ hydrochloric acid. These final dilutions were likewise distributed among small bottles, and analyzed within two hours after preparation. The standard solutions employed were all referred to the $N/10$ hydrochloric acid as a base, the caustic soda by direct titration, the iodine in the following manner: Solutions of potassium iodide, 5 per cent, and potassium iodate, 0.5 per cent, were prepared, and, appearing slightly alkaline, were neutralized after the addition of methyl red. Neither solution gave color when treated with acid and starch. On mixing 25 cc. of the two solutions, and adding starch, no color developed, but after adding one drop of $N/10$ hydrochloric acid to 25 cc. of the potassium iodate, then mixing with 25 cc. of the potassium iodide and lastly with starch, a pronounced blue appeared. The solutions having thus shown their neutrality, 25 cc. of the potassium iodide, 25 cc. of the $N/10$ hydrochloric acid from a pipette, and lastly 25 cc. of the potassium iodate, were placed in a 200 cc. Erlenmeyer flask. The solution was then immediately titrated with $N/10$ thiosulfate of proved neutrality, starch being added at the end. As the next step 25 cc. of the $N/10$ iodine were pipetted into 50 cc. of slightly acidified water contained in a 200 cc. Erlenmeyer flask and the solution was immediately titrated with the $N/10$ thiosulfate. In this way was obtained a direct comparison of the standard acid and iodine, which was a point of vital importance. Table III contains the results obtained, corrected to $N/10$ standard.

The reason that only duplicate results are given for the "reaction figures" is that methyl orange was employed for the others, this indicator being later rejected together with its results, in favor of the more sensitive methyl red.

In considering the results of Table III, it is necessary to note that the titrations were sometimes performed on different dilutions of the stock solution prepared at different times, and that we are dealing with a material of poor keeping powers. The figures on the same line in Columns V and VI should check.

Solution B, compared with Solution A, provided no chemical reaction other than neutralization has occurred, should show a "sulfide-base figure" of 24.17 +

2.50 = 26.67. The actual figure is 26.40, that is, 0.27 less. Likewise the "reaction figure" of Solution B should be $+2.50 - 1.01 = +1.49$, but being actually only $+1.20$, it shows a loss of 0.29, closely agreeing with the loss on the "sulfide-base figure."

TABLE III—TESTS OF METHODS ON LIME-SULFUR SOLUTIONS

Preparation of solutions	I Sulfide base figure; methyl orange	II Reaction figure	III Total iodine titration	IV Thiosulfate titration	V Sulfide-acid figure; Method A (I-II)	VI Sulfide-acid figure; Method B (III-IV)
A—Stock solution diluted with an equal volume of water..	24.20	-1.02	25.97	0.65		
	24.25	-0.99	25.88	0.65		
	24.15		25.95			
	24.07		25.93			
Mean,	24.17	-1.01	25.93	0.67	25.18	25.26
B—Stock solution diluted with an equal volume of $N/20$ NaOH.....	26.30	+1.17	26.01	0.85		
	26.50	+1.23	26.00	0.84		
	26.40		26.01	0.88		
	26.42		25.99			
Mean,	26.40	+1.20	26.00	0.86	25.20	25.14
C—Stock solution diluted with an equal volume $N/20$ HCl.	21.80	-3.10	25.71	0.65		
	21.74	-3.13	25.64	0.67		
	21.63		25.63	0.68		
	21.70		25.57	0.69		
Mean,	21.72	-3.12	25.64	0.67	24.84	24.97

The apparent loss is largely, at least, explicable through the formation of thiosulfate which has evidently occurred as shown by the figures for the thiosulfate titration.

Comparing the results for Solution C and Solution A, the former ought to show a sulfide-base figure of 21.67, while the actual figure found is 21.72, in good agreement. It ought also to show a reaction figure of -3.51, but actually shows only -3.12, a loss of 0.39. This loss is of course mainly attributable to the escape of hydrogen sulfide which is likewise shown by the loss of 0.29 in the total iodine titration.

Altogether the writer is unable to discover any fundamental weaknesses in the methods not inherent in most titration methods as executed under practical conditions. That the results in Columns V and VI, which represent the same value obtained by two distinct methods, do not show greater horizontal differences, in view of the character of the solutions operated upon and the number of titrations involved, must indicate the substantial accuracy of all the methods.

4. APPLICATION OF THE REACTION METHOD AND THE SULFIDE-ACID METHOD TO HYDROGEN SULFIDE SOLUTIONS—Inasmuch as Solution C of Experiment 3 showed the poorest check between the results of Columns V and VI, and since it was known that the reaction between sulfide and tetrathionate progresses normally only in alkaline solutions, it seemed that the methods could be given the severest test by attempting to apply them to a water solution of hydrogen sulfide. Therefore such a solution was freshly prepared in an amber bottle and diluted so that 50 cc. required about 10 cc. of $N/10$ iodine on direct titration. The tests tabulated in Table IV were then carried through in the order given.

The hydrogen sulfide solution evidently became significantly weaker between the successive tests. But the close agreement between the reaction figure

and the iodine titration in both Test B and Test C indicates that the methods are reliable when applied to solutions of hydrogen sulfide. In fact they made a better recovery of the hydrogen sulfide than the direct titration method, by the ratio of about 100 to 88.

TABLE IV—TESTS ON AQUEOUS HYDROGEN SULFIDE

Procedure	Reaction figure	Iodine titration
A—Into a 500 cc. Erlenmeyer flask containing 250 cc. water were poured from a cylinder 50 cc. of sample, starch added, and the liquid titrated at once.		9.06
B—Into a 500 cc. Erlenmeyer, neutral tetrathionate was prepared in usual way from 15 cc. $N/10$ I, 10 cc. of 10 per cent NH_4Cl being added. After diluting to 250 cc., 25 cc. of $N/10$ NaOH were introduced, followed by 50 cc. of sample. Stood three minutes before titration.	10.22	10.29
C—A repetition of B, except stood 6 minutes before titration.	10.09	10.05
D—A repetition of A.		8.72

Moreover, the iodine titration of the thiosulfate progresses decidedly more smoothly, rapidly and with a sharper end-point than the iodine titration of the original hydrogen sulfide. The method accordingly seems to offer promise in certain other estimations of soluble sulfides or hydrogen sulfide.

5. METHOD C FOR SULFIDE-ACID FIGURE—The sample was a diluted proprietary preparation. The factor for the thiosulfate solution against the $N/10$ iodine was found to be 0.997; therefore the factor for the tetrathionate solution was $0.499 \times N/10$.

TABLE V—COMPARISON OF SULFIDE-ACID FIGURES BY METHOD B AND METHOD C

Test No.	I Total iodine titration	II Thiosulfate titration	III Figure by Method B (I-II)	IV Tetra- thionate titration	V Figure by Method C (IV $\times$ 0.499)
1.....	23.82	0.98		45.5-45.7	
2.....	23.79	0.98		45.5-45.7	
Mean,	23.81	0.98	22.83	45.6 $\pm$ 0.2 = 45.8	22.85

An attempt was made to determine directly the correction for end-point thus: To 10 cc. of dilute ammonia (1 : 9) in a 100 cc. beaker was added from a capillary pipette 0.10 cc. of the same lime-sulfur solution; then 50 cc. distilled water were run in from a burette as in titration. The clear liquid was distinctly yellow and gave a plain positive test with nickel sulfate. There was then added 0.20 cc. of $N/20$ tetrathionate, after which a test with nickel sulfate yielded a positive result, but so faint that it is questionable whether it would have been detected in presence of the usual

amount of precipitated sulfur. After addition of 0.4 cc. tetrathionate the test with nickel sulfate was negative. A repetition gave an identical result. The theoretical titration would, of course, be 0.46 cc. It seems therefore that a correction of about 0.2 cc. $N/20$ tetrathionate may fairly be added to compensate for insensitiveness of indicator and slight oxidation which must necessarily result from the action of the air during titration.

Though Table V showed excellent results for Method C, there still remained the possibility that the method might not be trustworthy for solutions containing an excess of lime on account of possible appreciable decomposition of tetrathionate in alkaline solution before reaction with sulfide had gone to completion. Therefore 10 cc. portions of a lime-sulfur solution were titrated with tetrathionate after being diluted as follows: (a) with 10 cc. dilute ammonia, as in the regular method, (b) with 10 cc. concentrated ammonia, (c) with 10 cc. $N/10$ NaOH and 1 cc. concentrated ammonia. Several repetitions of the titrations gave exactly the same result for all, namely, an end-point between 52.5 and 52.7 cc. standard tetrathionate. Evidently the titration is entirely trustworthy when carried out on solutions strongly alkaline with ammonia, or alkaline to saturation with calcium hydroxide, the conditions produced under (c).

CONCLUSIONS

The methods described appear scientifically sound, being based on definite reactions and—assuming the absence of sulfites—involving no significant errors of which the source and probable magnitude cannot be estimated. They also appear practically applicable for use in the laboratory, some of them affording the desired information even for dirty dipping baths through which cattle and sheep have passed. The operations, though perhaps appearing numerous at first sight, are simple and rapidly executed when once the procedure has been grasped, while the standard solutions required are only those commonly at hand in all laboratories. Some of the methods appear to offer promise for the determination of hydrogen sulfide or compounds thereof in other materials.

BIOCHEMICAL DIVISION, BUREAU OF ANIMAL INDUSTRY
U. S. DEPARTMENT OF AGRICULTURE
WASHINGTON

LABORATORY AND PLANT

THE PRODUCTION OF AMMONIA FROM CYANAMID¹

By W. S. LANDIS

INTRODUCTION

After working for many years on the problem of the fixation of atmospheric nitrogen in the form of cyanides and cyanamides, the outbreak of the Boer War forced Professors Frank and Caro of Berlin to turn their attention to the utilization of their products otherwise than in the field of precious metal extraction. A consequence of the then existing economic situation was the discovery of the process of transforming the

¹ Presented at 8th Annual Meeting of the American Institute of Chemical Engineers, January 12, 1916, Baltimore, Maryland.

cyanamide compounds into ammonia. United States Patent No. 776,314, granted November 29, 1904, most probably represents the first American publication on this subject.

According to the specifications of this patent various cyanamide compounds and derivatives, including the crude form of the calcium salt sold under the name of Lime Nitrogen, when treated with steam or water in the proportion of three molecules of water to two atoms of the nitrogen in the cyanamide salt, will yield ammonia. It is recommended in the specifications that the reaction be carried out at temperatures from