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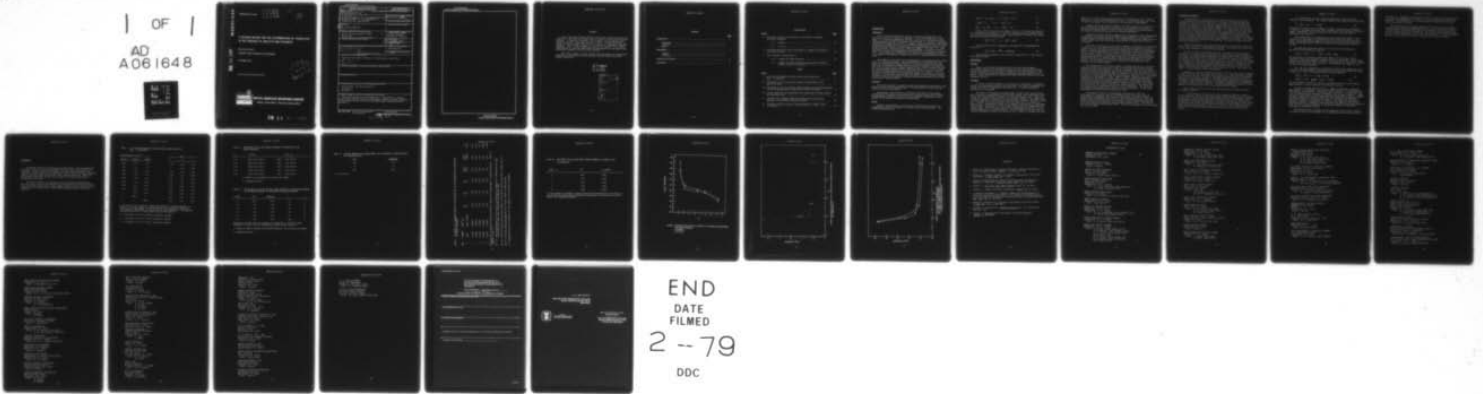
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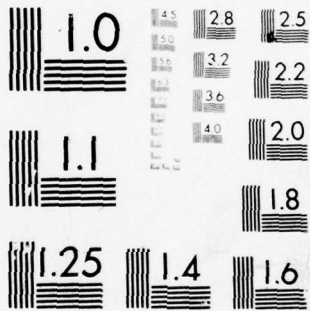
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**A REVISED METHOD FOR THE DETERMINATION OF THIOSULFATE
IN THE PRESENCE OF BISULFITE AND DITHIONITE**

WILLIAM P. KILROY

RESEARCH AND TECHNOLOGY DEPARTMENT

1 OCTOBER 1978

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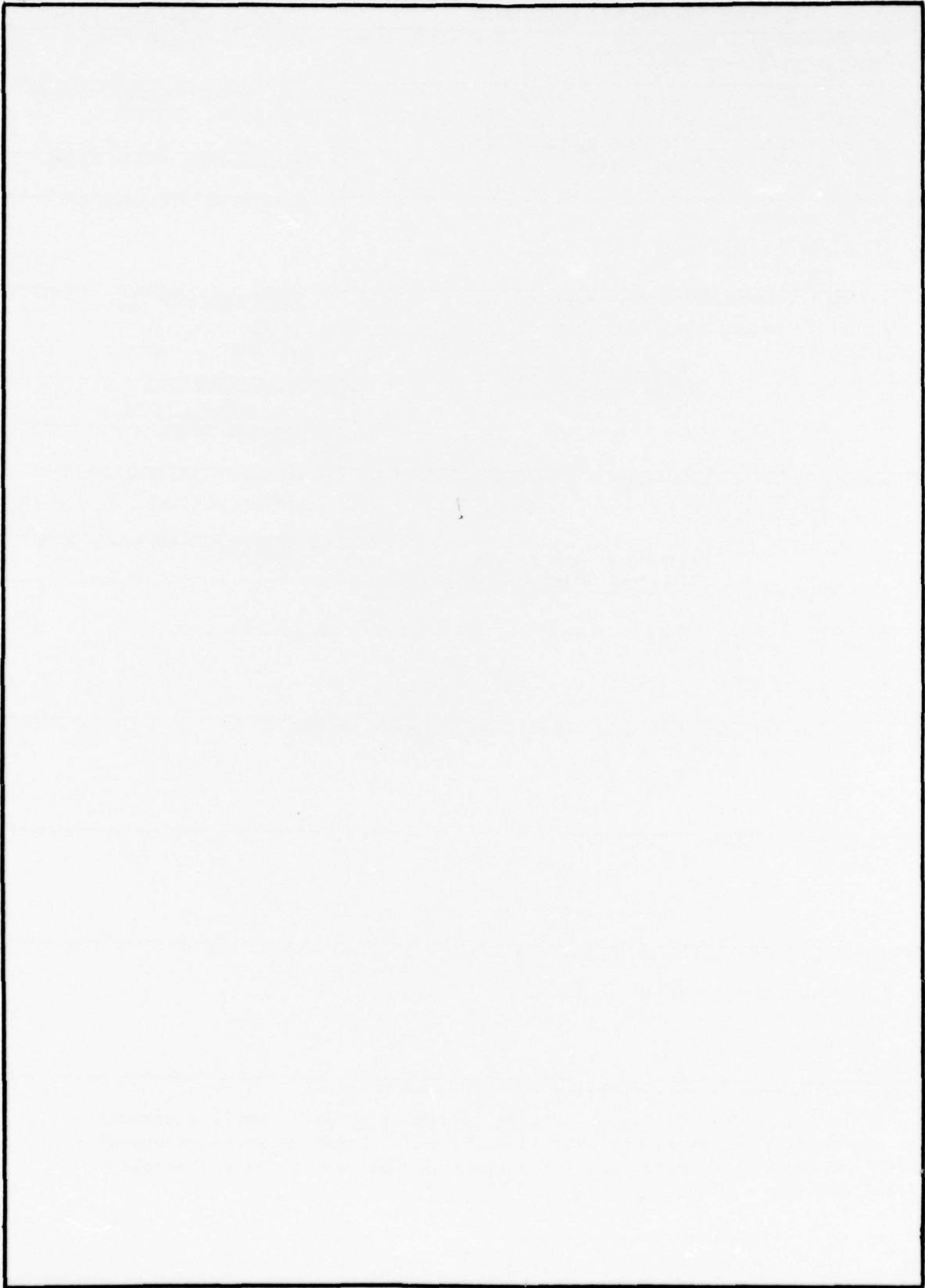
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SUMMARY

One of the high energy density batteries currently being considered by the Navy for future use in mines is the Li-SO₂ reserve battery. A question regarding the safety of this battery has recently arisen. This may be due, in part, to the fact that the nature of the cathodic reaction that occurs on discharge remains unknown. This is the second in a series of reports in a recent undertaking to develop experimental procedures for analyzing the discharge products of the Li-SO₂ battery.

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J. R. Dixon
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CONTENTS

	<u>Page</u>
INTRODUCTION	1
Background	
Objective	
Theory	
EXPERIMENTAL	2
Reagents	
Procedure	
DISCUSSION OF RESULTS	4
CONCLUSION	7

ILLUSTRATIONS

<u>Figure</u>		<u>Page</u>
1	The effect of pH on the % recovery of thiosulfate in buffered solutions containing	
	a) o 0.05M I ₂	13
	b) . 0.1 M I ₂	
2	Individual analyses of the % thiosulfate in a sample of dithionite as a function of pH	14
3	The % recovery of thiosulfate in	
	a) □ a sample of sodium dithionite	15
	b) o a sample of sodium dithionite containing an additional twofold increase in thiosulfate	

TABLES

<u>Table</u>		<u>Page</u>
I	pH of Various Mixtures of Sulfur Oxides after Oxidation in NaAc - I ₂ Solutions	8
II	The Effect of pH on the Percent Recovery of Thiosulfate in the Wollak Procedure	9
III	The Effect of pH of the Initial Iodine Oxidation in the Wollak Procedure on the Percent Recovery of Thiosulfate in Sodium Dithionite	9
IV	Percent Conversion of Tetrathionate into Thiosulfate by Excess Sulfide as a Function of pH	10
V	The Effect of a Standard Addition of Thiosulfate and pH on the Analysis of Thiosulfate in Sodium Dithionite	11
VI	The Effect of pH on the Total Iodine Consumed by a Sample (0.4g) of Dithionite	12

INTRODUCTION

Background

This is the second report in a series of current investigations in the analysis of mixtures of oxy-sulfur compounds. In the first report and a recent paper (1), it has been demonstrated that the first titer of the Wollak procedure (which determines the sum of dithionite and thiosulfate in a mixture of oxy-sulfur compounds) was susceptible to error if a sample containing dithionite, thiosulfate and bisulfite produces an acidic solution with $\text{pH} < 7$ when added to an aqueous formaldehyde solution neutral to Methyl Orange (as suggested by Wollak (2)). Under acidic conditions, thiosulfate reacts with formaldehyde. The rate of reaction is dependent on the pH, the formaldehyde concentration and the thiosulfate concentration. This problem can be eliminated by the addition of enough NaOH or Na_2CO_3 to the aqueous formaldehyde to maintain the pH of the sample-formaldehyde solution above 7.

The subject of this report is the determination of thiosulfate by the second titer of the Wollak procedure. Zocher and Saechtling (3) concluded that this method was unsatisfactory whereas Murooka (4) found the approach satisfactory. This titer of the Wollak procedure was also studied by Latimer (5) who reported difficulty in detection of a suitable endpoint in the iodine titration and found that the thiosulfate analysis could produce high results. This can occur when the initial oxidation takes place in a solution that is too acidic ($> 1\text{M H}^+$), a situation that can develop if the thiosulfate content of a mixture is less than 10 percent. On the other hand, Zubritsky and Danehy (6) have recently reported analysis of mixtures of oxy-sulfur compounds using Wollak's method and have found the procedure "unexceptionable".

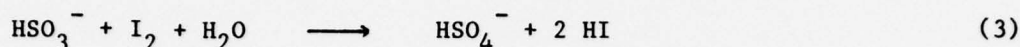
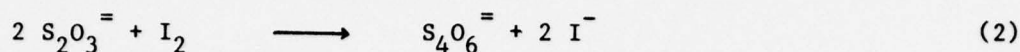
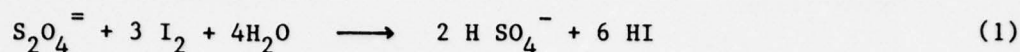
Objective

Due to the diversity of reports concerning the analysis of thiosulfate, the Wollak procedure has been reinvestigated. The experimental procedure has been found to be totally unacceptable.

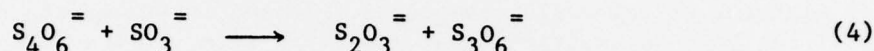
The purpose of this report is to illustrate the nature of the problem encountered in the analysis of thiosulfate by the Wollak method and to develop an experimental procedure by which an accurate analysis of thiosulfate can be obtained in the presence of dithionite and bisulfite.

Theory

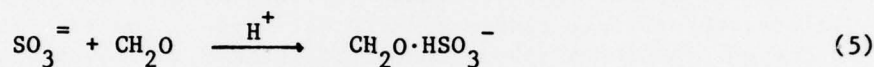
Analysis of thiosulfate in the presence of dithionite and bisulfite is accomplished by adding the mixture to an acidic excess iodine solution. The following reactions occur.



Excess sulfite solution is then added in order to (a) remove any unreacted I_2 in accordance with equation (3), and after adjusting the pH to between 8 and 10; (b) convert the tetrathionate, $\text{S}_4\text{O}_6^{=}$, quantitatively to one-half the original thiosulfate according to the reaction



The unreacted sulfite is complexed by the addition of formaldehyde and acetic acid.



The thiosulfate produced by the reaction of equation (4) is then titrated with standard iodine.

EXPERIMENTAL

Reagents

Reagent grade chemicals and distilled water were used throughout. Thiosulfate solutions were standardized before use using standard KIO_3 solution and the thiosulfate was in turn used to standardize the iodine solutions. The sulfite solution was prepared without deairation and was approximately 10% (0.8 molar). Sodium acetate as the trihydrate and Baker purified dithionite were used throughout the work.

Procedure

In theory, the Wollak method for the analysis of thiosulfate is acceptable. However, the experimental procedure has been found to be totally unacceptable for reasons which will be enumerated in the discussion. A revised experimental procedure is now described.

Add 0.4g of a thiosulfate-containing sample through a dry long stem funnel into a solution of approximately 73 ml of excess aqueous iodine containing a minimum of 3g of sodium acetate trihydrate in a 100 ml volumetric flask. (70 ml of ~0.10M I_2 is generally sufficient for ~0.4g dithionite sample). The sample should be added slowly over a one-half minute interval while constantly swirling the solution. Transfer any residue from the funnel with about 2 ml of a similar I_2 - NaAc solution. The unreacted iodine is now removed by the addition of 0.8M Na_2SO_3 solution and an additional 8 to 10 ml of the sulfite solution is immediately and rapidly added. The solution is neutralized to phenolphthalein (pH 8 to 10) with dropwise addition of a 10M NaOH solution. After standing for 5 minutes, add 4 ml of 37% formaldehyde and about 5 ml 20% acetic acid. Dilute to the mark with water.

Remove a 25 or 50 ml aliquot, adjust the pH to 4 with 20% acetic acid. Using a microburet, titrate with 0.005M standard iodine to a sharp starch end point. The end point will appear violet colored due to the presence of formaldehyde.

Sodium acetate was originally added to the iodine solutions to control the pH and prevent the decomposition of dithionite by the hydriodic acid produced. The interrelationship among the sodium acetate concentration, pH and the percent thiosulfate recovered was studied by the following experiments.

Mixtures of various oxy-sulfur compounds were prepared by adding known amounts of anhydrous sodium bisulfite and anhydrous sodium thiosulfate to a previously analyzed sample of sodium dithionite. The preweighed mixtures were added to excess standard iodine solutions containing various amounts of sodium acetate and the pH recorded.

The effect of pH on the initial iodine oxidation of thiosulfate was determined by adding 0.1 to 0.3g anhydrous thiosulfate to pH adjusted solutions of excess iodine. The pH of the iodine solution was adjusted by the addition of appropriate amounts of either hydrochloric acid, acetic acid-acetate buffer or sodium acetate to give a total volume of 50 ml of 0.05M or 0.1M iodine. The effects of pH on the thiosulfate recovered in mixtures of oxy-sulfur compounds were determined by adding known amounts of analyzed sodium dithionite and sodium dithionite-thiosulfate mixtures to excess iodine solutions containing various amounts of sodium acetate. In both studies, the percent recovery of the thiosulfate was then determined by the revised method.

The decomposition of dithionite appears to produce sulfide (2,7), and since formation of sulfur also occurs at low pH, it was decided that several sulfide reactions should be investigated as a possible explanation for the sulfur formation and the high thiosulfate analysis that occurs at low pH. Since the reaction of sulfide with various constituents might be competitive with the oxidation of sulfide by iodine, the study was made under the most favorable conditions, i.e., with excess sulfide and in the absence of iodine. Excess ultrapure sodium sulfide from an unopened bottle was added to a known amount of sodium tetrathionate (99% pure) dissolved in various acid solutions of differing pH. The reaction was allowed to proceed five minutes and excess cadmium chloride was then added. The sulfide was filtered and the filtrate titrated with standard 0.05M I_2 . The iodine titer was corrected for the oxidizable impurity in the tetrathionate. The experiment was repeated using sodium sulfite in place of the tetrathionate. In this case, formaldehyde was added before titrating with iodine.

A pH dependent reaction of formaldehyde bisulfite with iodine was investigated as a possible cause of the fading end point previously reported. Known amounts of anhydrous sodium bisulfite were added to aqueous solutions containing excess formaldehyde (4 ml total) in 100 ml volumetric flasks. Water was added to the mark, 25 ml aliquots were withdrawn, starch indicator added and the pH of each aliquot was buffered at various values between 4 and 7. The aliquots were titrated using 0.005M standard iodine. Acidified formaldehyde was also titrated for use as a blank.

DISCUSSION OF RESULTS

The determination of thiosulfate by the Wollak method has been found to be unacceptable for the following reasons. The major problem arises when one attempts to titrate the final solution. A 0.2g sample of sodium dithionite was analyzed for thiosulfate by the method suggested by Wollak (2) and recently by Zubritsky and Danehy (6). Using 0.05M standard iodine as titrant, the end point occurs on the addition of a few drops of iodine. If 0.005M iodine is used, then the end point is not detectable due to dilution of the iodine in the large volume of solution (8), combined with the presence of formaldehyde which hinders the detection of the starch-iodine end point. In addition, the one gram of sodium acetate originally added to prevent the acid decomposition of dithionite is insufficient in samples containing relatively large amounts of dithionite. The revised experimental procedure eliminates these problems, including the fading end point previously reported (5).

Table I shows the pH to be expected when mixtures of oxidizable sulfur are added to various iodine - sodium acetate solutions. The hydrogen ion is generated by the iodine oxidation of bisulfite and dithionite.

The initial step of the Wollak titration, including the revised method, is equivalent to a titration of the thiosulfate by iodine under various conditions of acidity, the acidity being determined by the composition of both the sample and the I_2 -NaAc oxidizing solution. The effect of pH on the recovery of thiosulfate is illustrated in Figure 1 and tabulated in Table II. The low recovery that occurs at the higher pH is attributable to the partial oxidation of thiosulfate to sulfate (8). Although the literature indicates quantitative recovery of thiosulfate in excess iodine solutions (concentration not reported) with pH as low as -0.5 (9), Figure 1 shows that high thiosulfate recovery can occur at pH~1. This may be the result of using different iodine concentrations.

Analysis of a sample of sodium dithionite followed the same course of behavior as when thiosulfate was oxidized by acidic iodine, i.e., high thiosulfate recovery in solutions of low pH. The results are tabulated in Table III and the individual analyses are illustrated in Figure 2. The high standard deviation at low pH is indicative of the unpredictability of the analysis when insufficient sodium acetate is present. High thiosulfate analyses is invariably accompanied by the formation of sulfur during the initial oxidation. Although unconfirmed, the amount of sulfur appeared to be proportional to the excess thiosulfate that formed.

Some of the potential causes of the high thiosulfate and sulfur formation were briefly examined.

i) The intensity of the yellow color that appears on addition of excess sulfite during the removal of the excess iodine was pH dependent being most intense at low pH (0.2) and increased with iodine and/or bisulfite concentration. However, sulfite added to dithionite samples did not affect the recovery of thiosulfate. In addition, sulfite that was allowed to react with excess sulfide in acidic iodine of pH 0.8 did not produce any thiosulfate. Neither the yellow complex nor sulfite under acidic conditions appears to be a direct factor. Latimer has shown that a sulfur-sulfite reaction cannot quantitatively account for increases in thio-sulfate.

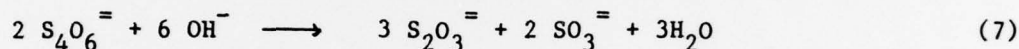
ii) Tetrathionate, the only reactive oxidant that forms from iodine oxidation, was investigated. The reaction between excess sulfide and tetrathionate



was studied at various pH in the absence of iodine. The results are tabulated in Table IV. Although sulfur does form, increasing pH favors reaction of tetrathionate. Consequently, the high thiosulfate that occurs at low pH cannot be explained by this reaction.

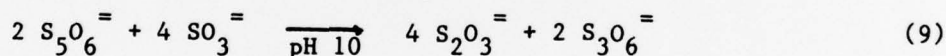
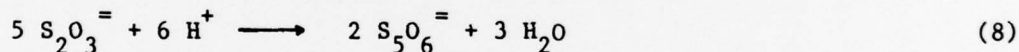
Acid decomposition of tetrathionate in excess iodine was examined. After oxidation of a 0.4g sample of sodium dithionite in excess 0.1M iodine solution (pH~4), concentrated HCl was added until the pH was 0.8. No sulfur formed and the percent thiosulfate found (2.48%) was similar to the oxidations that occurred at pH~4.

Although high thiosulfate analysis correlates with low pH oxidation, hydrolysis of tetrathionate at high pH



and hydrolysis of trithionate produced upon addition of the excess sulfite (reaction 5) have been reported as possible sources of thiosulfate. However, the analytical procedure was found to tolerate large variations in both time of standing and the pH of the excess sulfite solutions. Tetrathionate was judged not to be a cause of the high thiosulfate.

iii) The acid decomposition of thiosulfate, which occurs competitively with oxidation, has been proposed as an explanation of the high thiosulfate that occurs at low pH (9). This is illustrated by the following equations:



The stoichiometric recovery of 4 moles of thiosulfate for every 5 moles added is higher than the 1:2 ratio predicted by the Wollak titration.

In order to examine this possibility, a sample of dithionite, containing approximately 2.5% thiosulfate, was analyzed in the presence of an additional two-fold increase in thiosulfate. The data are shown in Table V. If equations 8 and 9 are the explanation for increased thiosulfate, then one might expect still larger increases in thiosulfate at low pH when additional thiosulfate is present. Comparison of the analysis of dithionite (Table III) and dithionite with additional thiosulfate (Table V) is illustrated in Figure 3. No significant difference is observed. Thiosulfate concentration in itself does not appear to be the major contributing factor. In addition, when thiosulfate samples (analyzed and reported in Table II) were increased threefold, no significant variation in the percent thiosulfate recovered was detected.

Thiosulfate recovery increases with decreasing pH whereas sulfite oxidation in iodine was found to be independent of pH, giving the same recovery at pH 0.25

as at pH 5.15. Consequently, the results of Table VI show that increasing acidity allows some acid decomposition of dithionite to occur competitively with iodine oxidation. Stoichiometrically, the acid decomposition products of dithionite require less iodine at low pH.

The fading end point previously reported is the result of a pH dependent reaction between iodine and formaldehyde bisulfite. The end point of a bisulfite ($\sim 10^{-3}M$) solution containing excess CH_2O (4 ml 37% CH_2O in 100 ml) titrated by 0.005M I_2 fades rapidly with increasing pH. The end point fades rapidly at $pH > 6$ and the precision of analysis is poor if the pH approaches 6.0. Good reproducible analyses can be performed if the pH is adjusted to 4.0 before titrating.

CONCLUSION

The Wollak titration of thiosulfate has been revised. The new experimental procedure eliminates the numerous problems cited and allows correct analysis of thiosulfate in the presence of large amounts of other iodine oxidizable sulfur compounds. Several reactions were examined in order to explain the high thiosulfate analysis that occurs when the pH of the iodine solution is too low. There are many plausible reactions but time did not permit a conclusive quantitative explanation at this time.

The third titration of the Wollak procedure has also been investigated. When thiosulfate, bisulfite and dithionite are simultaneously oxidized by iodine, sufficient sodium acetate must be added (minimum pH~4) in order to minimize acidic decomposition of dithionite which would compete nonquantitatively with iodine oxidation.

TABLE I. pH OF VARIOUS MIXTURES OF SULFUR OXIDES AFTER OXIDATION IN NaAc - I₂ SOLUTIONS.

Sulfur Oxide, Wt. % *			pH		
Na ₂ S ₂ O ₄	Na ₂ S ₂ O ₃	NaHSO ₃	A	B	C
89.9	2.5	6.9	1.97	1.02	3.92
85.1	7.6	6.5	--	1.10	3.99
68.6	24.9	6.0	3.54	1.21	4.29
68.6	6.0	24.9	2.30	1.11	4.08
49.8	44.8	5.0	4.23	1.54	4.62
49.8	5.0	44.8	2.87	1.13	4.19
10.0	79.7	10.0	5.12	4.62	5.36
10.0	10.0	79.9	3.93	1.39	4.43
--	50.0	50.0	4.68	3.65	4.93
--	100.0	--	6.99	7.06	7.26
--	--	100.0	3.83	1.32	4.40

* The mixtures were prepared by adding known amounts of anhydrous Na₂S₂O₃ and NaHSO₃ to an analyzed sample of sodium dithionite containing 89.9% Na₂S₂O₄, 2.53% Na₂S₂O₃, 6.88% NaHSO₃ and calculating the final composition. The remaining composition consists of a small formate and chloride impurity.

A - 0.2g sample in 75 ml of 0.05M I₂ containing 1.0g NaAc

B - 0.4g sample in 75 ml of 0.1M I₂ containing 1.0g NaAc

C - 0.4g sample in 75 ml of 0.1M I₂ containing 3.0g NaAc

TABLE II. THE EFFECT OF pH ON THE PERCENT RECOVERY OF THIOSULFATE IN THE WOLLAK PROCEDURE.

pH	0.05M I ₂	0.1M I ₂
0.15	103.7 (n=2, S=0.3)	105.2 (n=4, S=1.0)
1.10	100.9 (n=2, S=0.3)	100.4 (n=2, S=0.3)
3.35	100.2 (n=2, S=0.6)	99.9 (n=2, S=0.6)
4.76	99.8 (n=3, S=0.4)	99.7 (n=3, S=0.4)
7.26	98.6 (n=5, S=1.0)	98.2 (n=3, S=0.4)

n = number of 0.1g samples (3 titrations per sample)

S = standard deviation

TABLE III. THE EFFECT OF pH OF THE INITIAL IODINE OXIDATION IN THE WOLLAK PROCEDURE ON THE PERCENT RECOVERY OF THIOSULFATE IN SODIUM DITHIONITE.

g NaAc	pH*	%Na ₂ S ₂ O ₃	S	n
0	0.80	4.35	.37	6
1.0	1.01	3.20	.40	17
1.5	1.27	2.74	.16	5
2.0	1.69	2.67	.19	8
3.0	4.00	2.53	.11	6
4.0	4.36	2.52	.054	5

*Average pH recorded after the oxidation of a known mass (~0.4g) of sodium dithionite in 75 ml of 0.1M I₂ containing the grams of NaAc indicated.

n = number of samples analyzed (revised Wollak method), two titrations per sample

S = Standard deviation

TABLE IV. PERCENT CONVERSION OF TETRATHIONATE INTO THIOSULFATE BY EXCESS SULFIDE AS A FUNCTION OF pH*

<u>pH</u> *	<u>% REACTION</u>
0.8	1.3
1.0	6.4
4.8	93.0

* ± 0.1 pH unit

TABLE V. THE EFFECT OF A STANDARD ADDITION OF THIOSULFATE AND pH ON THE ANALYSIS OF THIOSULFATE IN SODIUM DITHIONITE.

NaAc	AVERAGE	MASS* (g)	pH (1)	pH (2)	pH (3)	%S ₂ O ₃ ⁼ Total	%S ₂ O ₃ ⁼ in S ₂ O ₄ ⁼	S (n=4)
g	S ₂ O ₄ ⁼	S ₂ O ₃ ⁼ (anhyd)						
0	0.4029	0.02244	0.82	0.78	1.35	9.44	4.40	1.03
1	0.3998	0.02254	1.04	0.95	2.00	8.56	3.40	0.65
2	0.4025	0.02306	1.68	1.51	4.05	7.84	2.56	0.12
3	0.4030	0.02264	3.96	3.77	4.48	7.62	2.43	0.051
4	0.4021	0.02242	4.39	4.30	4.73	7.54	2.40	0.029

*Average mass of anhydrous sodium thiosulfate added to an average mass of sodium dithionite. Number of samples, n, was 4.

pH (1) - pH of approximately 75 ml of 0.1M I₂ containing X g of NaAc after adding both the S₂O₄⁼ containing X g of NaAc after adding both the S₂O₄⁼ and S₂O₃⁼.

pH (2) = pH of the above solution after removal of the excess iodine with sulfite (0.8M) solution

pH (3) = pH after adding approximately 10 ml excess sulfite (0.8M) solution.

S = standard deviation for analysis of four samples, two titrations per sample.

TABLE VI. THE EFFECT OF pH ON THE TOTAL IODINE CONSUMED BY A SAMPLE (0.4g)
OF DITHIONITE*

NaAc, g	pH	I ₂ , mmoles
0	0.92	6.381
1	1.15	6.410
2	1.80	6.434
3	3.94	6.443
4	4.38	6.449

* Three samples of 0.4000g of sodium dithionite were oxidized by 75 ml 0.1M I₂ at each pH and the average iodine consumed was determined by titrating the unreacted iodine with standard thiosulfate.

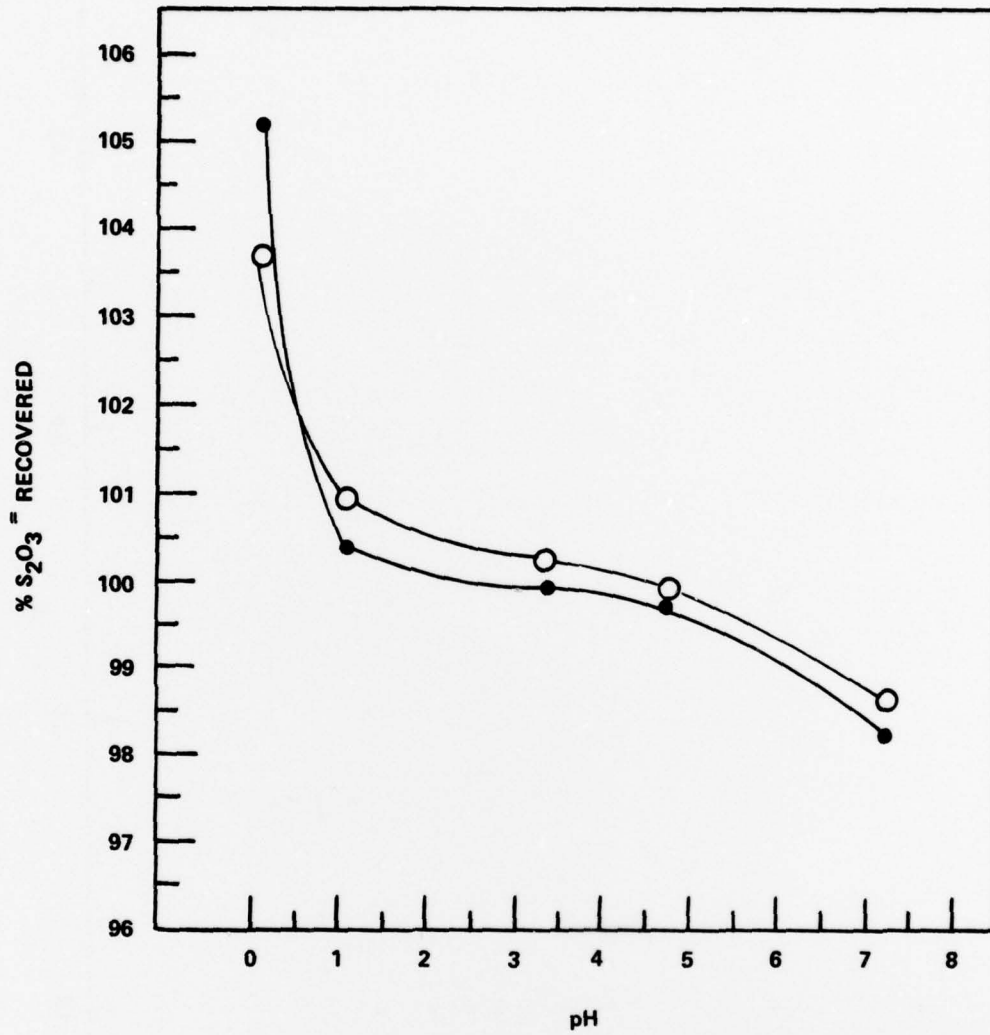


FIGURE 1 THE EFFECT OF pH ON THE % RECOVERY OF THIOSULFATE IN BUFFERED SOLUTIONS CONTAINING
a) ○ 0.05M I₂
b) ● 0.1M I₂

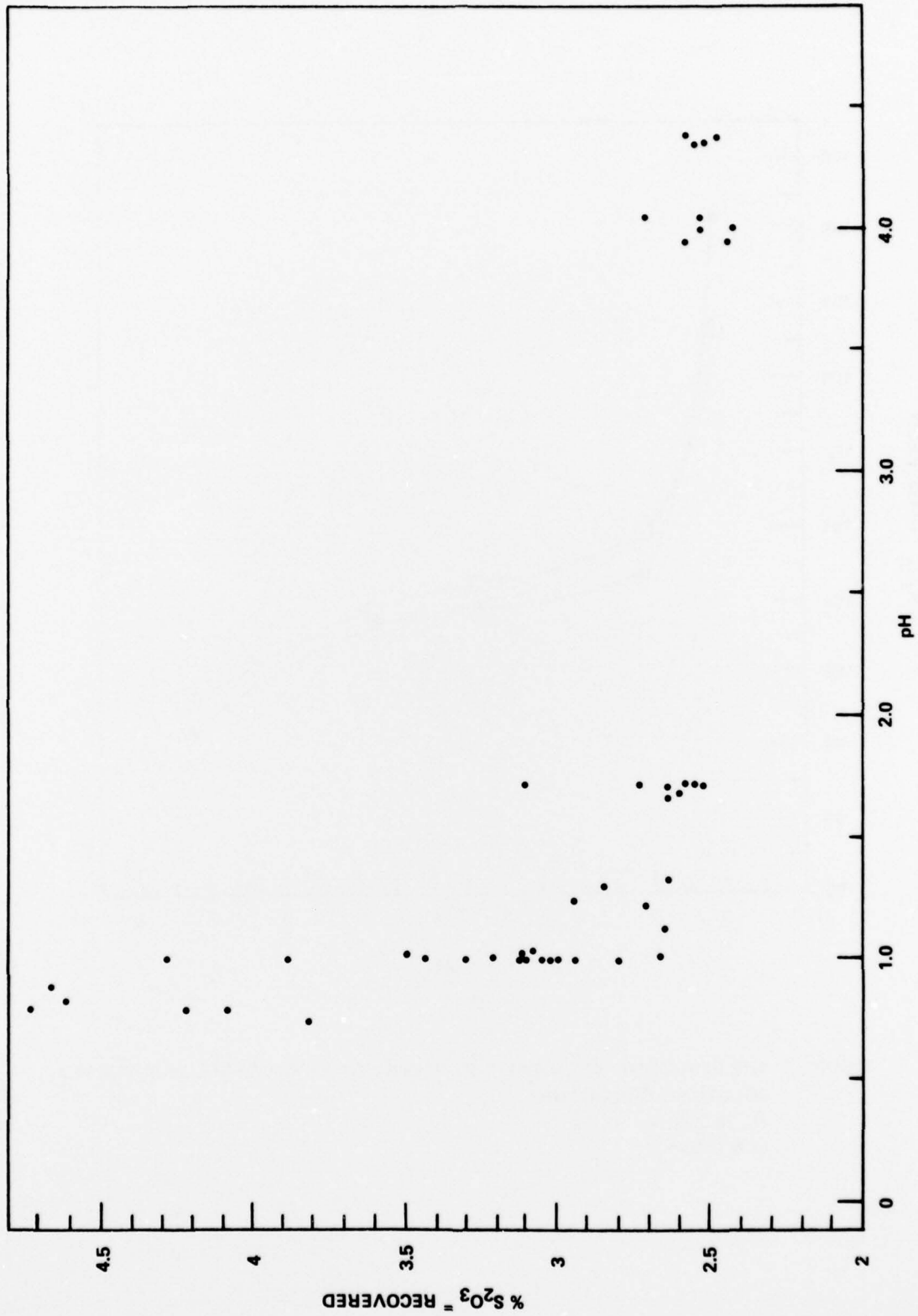


FIGURE 2 INDIVIDUAL ANALYSES OF THE % THIOSULFATE IN A SAMPLE OF DITHIONITE AS A FUNCTION OF pH

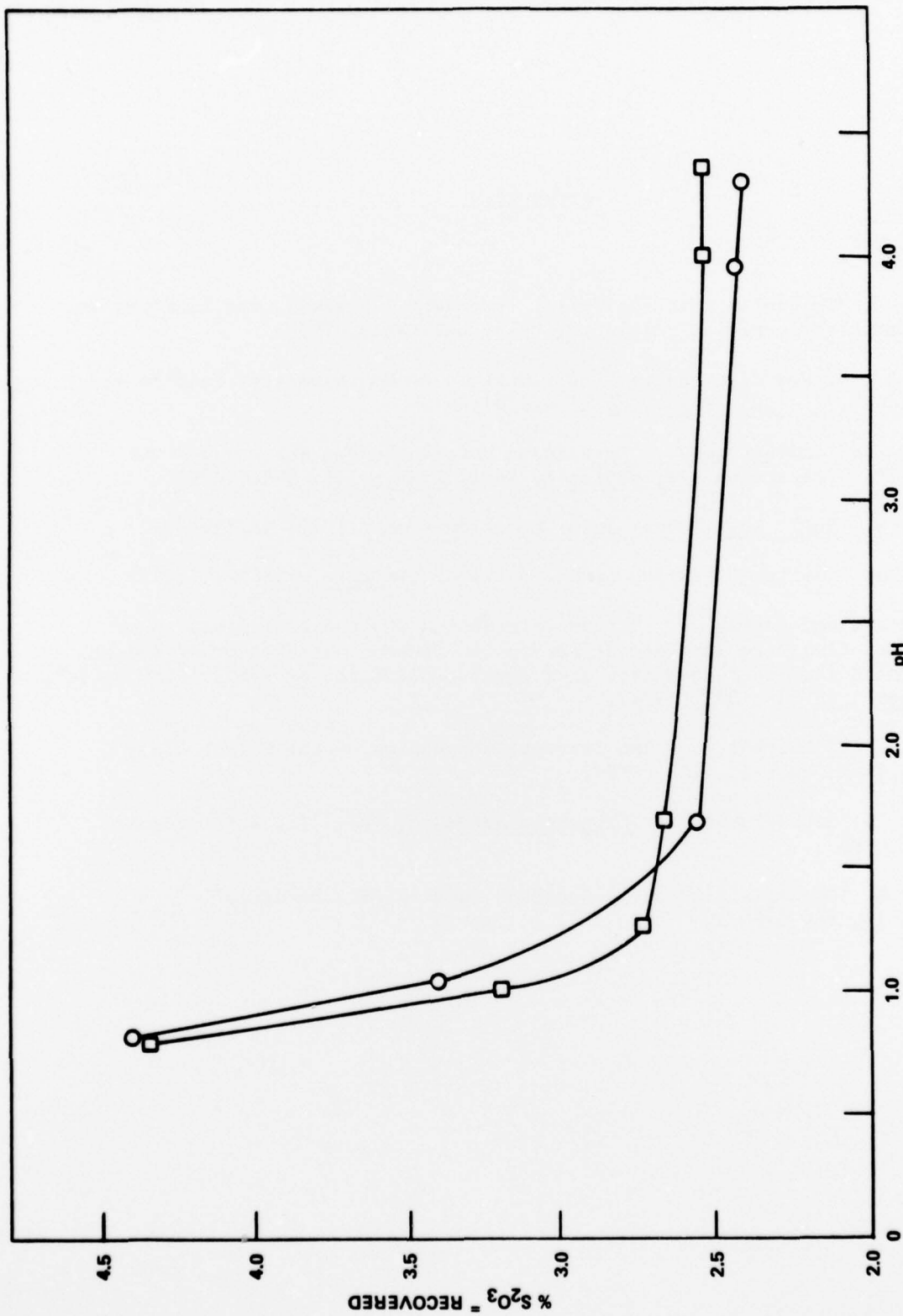


FIGURE 3 THE % RECOVERY OF THIOSULFATE IN
a) □ A SAMPLE OF SODIUM DITHIONITE
b) ○ A SAMPLE OF SODIUM DITHIONITE CONTAINING AN ADDITIONAL
TWOFOLD INCREASE IN THIOSULFATE

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