

Losses of Sulfur
from the
Sulfate Paper Pulp Process

Thesis
by
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INTRODUCTION

In the manufacture of paper pulp from wood by the kraft process, wood chips are heated or digested with a solution of Na_2S and NaOH in order to extract the more reactive organic compounds from the less reactive, and therefore more durable and desirable, cellulose. The primary source of Na_2S is Na_2SO_4 which is reduced to Na_2S by C at a high temperature, and the primary source of NaOH is Na_2CO_3 which is converted to NaOH by reacting with CaO and settling out the resultant CaCO_3 . The inorganic constituents in the solution containing the material extracted from the wood are recovered by evaporating the water and burning the organic matter. The burning is done in a reducing atmosphere so that carbon formed by the decomposition of the organic matter can reduce make-up Na_2SO_4 and other inorganic sulfur compounds to Na_2S , and at a high enough temperature so that the Na_2S and Na_2CO_3 formed, melt and run out at the bottom of the furnace. Here they are dissolved in water, Make-up Na_2CO_3 is added, then the proper amount of CaO . The resultant CaCO_3 is settled out to give the solution desired. An attempt to remove sulfur and sodium compounds from the flue gases is made by scrubbing them either with the alkaline liquor from the digestors or with water.

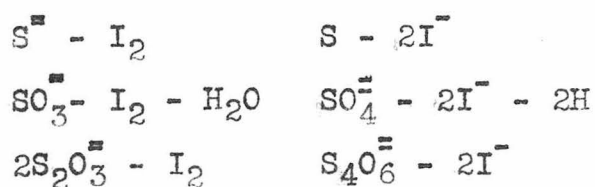
The object of this research is to investigate the relative losses of sulfur and sodium compounds from the system with the object of using a mixed double salt, $\text{Na}_2\text{CO}_3 \cdot 2\text{Na}_2\text{SO}_4$ and $2\text{Na}_2\text{CO}_3 \cdot 3\text{Na}_2\text{SO}_4$, to replace losses instead of Na_2CO_3 and Na_2SO_4 separately. This double salt could be used at present ~~in~~ with Na_2SO_4 in making up losses but since the ratio of Na_2SO_4 to Na_2CO_3 used at present is about 10/1, only a small proportion of the double salt could be used. If losses of sulfur compounds from the system could be decreased a smaller ratio of Na_2SO_4 to Na_2CO_3 could be used in making up losses and a larger proportion of the double salt could be used. Consequently, the investigation has been one of the sulfur compounds found in the system and their reactions with regard to possible losses.

Previous Work

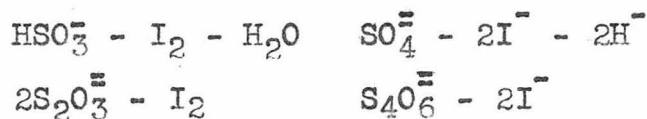
The standard system of analysis used by the paper making industry has been developed by Otto Kress of the Forest Products Laboratory at Madison, Wisconsin. (1)

This System of analysis is used with solutions containing no organic matter and no polysulfide. The parts relating to sulfur compounds are given briefly as follows:

To determine S^{\equiv} - SO_3^{\equiv} - $\frac{1}{2}S_2O_3^{\equiv}$ titrate a portion with I_2 in basic solution almost to the end point, acidify with acetic acid, and continue the titration to the starch end point. The reactions are



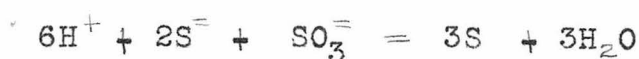
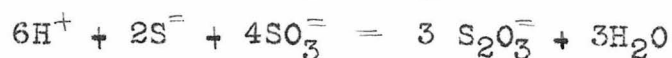
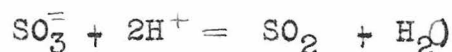
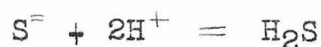
To determine SO_3^{\equiv} and $S_2O_3^{\equiv}$ precipitate S^{\equiv} with ammoniacal $ZnCl_2$, dilute to a given volume, allow the ZnS to settle, and take an aliquote part for titration. Neutralize to the methyl orange end point, titrate to the starch end point with I_2 , and neutralize again to the methyl orange end point. SO_3^{\equiv} is distinguished from $S_2O_3^{\equiv}$ by the fact that it liberates acid when oxidized with I_2 . The reactions are:



To determine SO_4^{\equiv} . acidify a portion with HCl , boil to

(1) Paper, 17, No. 24, 30 (1916)

expel H_2S and SO_2 , and determine SO_4^- by precipitating and weighing as BaSO_4 in the usual way. The reactions are:



G. C. McNaughton of the Forest Products Laboratory tested the following method of determining S^- in the black liquor produced by the action of the $\text{Na}_2\text{S} - \text{NaOH}$ solution on wood. Titrate the diluted liquor with ammoniacal ZnCl_2 determining the end point by testing a portion of the solution for S^- with ammoniacal NiSO_4 on a spot plate.

Griffin⁽²⁾ recommends the following procedure for the determination of SO_4^- in black liquor. Dilute to about 125 , acidify, heat to boiling, precipitate the SO_4^- as BaSO_4 , filter, and ignite in a platinum crucible.

Although a great deal of work has been done on the effects of various liquor variables on the yields and properties of the pulp produced, very little has been done on the products of reaction. The active constituents are NaOH and Na_2S ; Na_2SO_4 and Na_2CO_3 having little, if any effect.

According to Heuser⁽³⁾ only a comparatively small percentage of Na_2S is used up in the pulping of beechwood,

(2) Technical Methods of Analysis - Second Edition

(3) Wochbl. Papier-Fabr. 1913 p. 2209 (from Sutermeister)

about 20% to 25%. Klason and Segerfeld⁽⁴⁾ found that of the original sulfide in the liquor 51.8% was combined with lignin, 15% expelled as volatile compounds, 16.4% remained as sulphide, and 16.4% was unaccounted for.

According to Falk⁽⁵⁾ the following compounds are obtained by condensing the steam produced by releasing the pressure from the digestors at the end of a cook.

	Oily Portion	Aqueous Portion
	Kgs./ton pulp	Kgs/ton pulp
Mercaptan	.062	.06
Dimethyl sulphide	.927	.17
Dimethyl disulphide	.103	.05
Turpentine	8.49	.92
Distillation residues	.721	---
Methyl alcohol	---	5.00

Klason⁽⁶⁾ has analyzed the flue gases from the smelting furnace and has found 13 mg. methyl mercaptan and 4 mg. hydrogen sulphide per cubic meter.

The most reliable work on the reduction of Na_2SO_4 to Na_2S has been done by Budnikov⁽⁷⁾. In his latest article on this subject he draws the following conclusions:

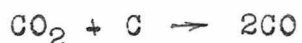
(1) The production of Na_2S by the reduction of Na_2SO_4 rests upon the following three principal reactions:

(4) Papier Fabr., 1911 9, 1093-99 (from Sutermeister)

(5) Papier Fabr., 1909 7, 469-72 (from Sutermeister)

(6) Papier Ztg., 1908 33, 3619 (from Sutermeister)

(7) Zeit fur anorg und allgem Chemie, 170, 225-7



(2) The temperature of the beginning of reaction depends on the purity and density of the carbon and upon its mixture with sodium sulfate. The reduction occurs first between the solid phases.

(3) The velocity of the reaction is great and continues only for fractions of minutes.

The lowest temperatures for the beginning of reaction found by him were 300°C, 750°C, 880°C, and 750-800°C for sugar carbon. The following table represents the sort of data obtained:

No.	Temp.	Min.	Sec.	Weights		% Yields		
				Na ₂ SO ₄	C	%Na ₂ S	%Na ₂ SO ₃	%Na ₂ SO ₄
1	800	20	---	.2	.06	80.0	---	---
2	850	4	---	.6	.2	95.0	trace	trace
3	880	4	---	.6	.2	92.2	---	---
4	1000	1	10	.6	.12	61.5	1.15	---
5	1000-1100	---	40	.6	.15	88.6	trace	1.22

In this experiment the gases given off were not analyzed but gas analyses from other experiments show mostly CO₂. Air was displaced by nitrogen from the electric furnace used, the temperatures were measured by a platinum platinum-rhodium thermocouple, and the Na₂S was determined by dissolving and precipitating as Ag₂S with ammoniacal AgNO₃.

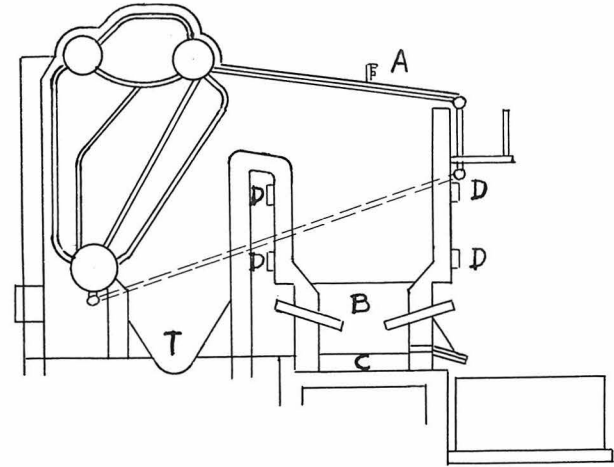
Budnikov did not attempt to account for all of the sulfur in the original Na_2SO_4 . However, the gases which he obtained always gave a precipitate with AgNO_3 , which he ascribed to the presence of COS . The presence of a side reaction between sodium sulfate and sulfide was proven as follows: 13g of Na_2S (prepared by calcining the hydrated salt in a current of hydrogen) mixed with .26g of Na_2SO_4 was heated at 850° for 40 min. and .0519 g of SO_2 absorbed in an iodine solution. This corresponds to 44% of the SO_2 in the Na_2SO_4 . The side reactions suggested by Budnikov as the ones which reduce the yield of Na_2S are:



The most complete published information on the operation of the recovery system as a whole is given by Wagner⁽⁸⁾ for the operation of the Wagner furnace, and inasmuch as this system has been the one studied a somewhat detailed description will be given. The liquor is evaporated to about 70% solids in triple or quadruple effect evaporators and sprayed into the furnace at A. As it falls to the reducing zone, B, it is further evaporated

(8) Ind. and Eng. Chem. 22, 1930, 122.

and the organic matter partly decomposed by the hot gases arising from the reducing zone. The bed of charred organic matter, B, is about 5 ft. thick and the pool of molten



Na_2SO_4 and Na_2CO_3 , C, is about 1 ft. thick. Air nozzles project into the reducing zone and the air injected by them burns excess carbon, generating the heat necessary for the endothermic reduction of Na_2SO_4 to Na_2S . The inorganic salts run down into the pool, C, and out through a spout into a tank containing water. The gases in the furnace are burned by secondary air which is introduced into the furnace at points D. They pass through the waste heat boiler shown, and into a scrubber. This scrubber consists of a cyclone separator into which is introduced an exceedingly fine spray of scrubber liquor, the particles of spray being approximately the same size as the colloidal sized salt particles with which they unite. Part of the liquor is collected by the cyclone separator and the remaining part is recovered by passing the gases over baffles and through a layer of Hexahelix tile. All gases produced in the plant

containing odorous organic sulfur compounds are added to the furnace with the secondary air and burned. Scrubber liquor is circulated through the trough, T, in the boiler in order to carry out any particles which settle into this part. The scrubber liquor is removed continuously from the scrubber system and added to the initial or "cooking" liquor either before or after it has been used to remove non-cellulose matter from the wood.

The efficiency of the system in recovering inorganic salts from the black liquor injected into the furnace is primarily dependent upon the efficiency of the scrubber in removing these salts from the flue gases. The amount of salts carried over into the scrubber in the flue gases is a function of the type of spraying done; hence it is necessary to regulate the spray closely. Recently, it has been found that a Cottrell precipitator works well at moderate cost in removing solids from the flue gases. Also bag filters have been found to work well. The temperatures given for the most efficient operation are as follows:

Upper zone	1050 - 1150 C
Lower zone	900 - 1050 C
Emerging smelt	850 - 1000 C

The chemical reactions in the furnace are discussed by Wagner as follows; "The chemical reactions occurring in this process are similar to that in the smelter process, with this exception. In the rotary of the old process the low temperature and excess carbon cause sulfide and other sulfur compounds to change to carbonates and sulfur dioxide, the latter being carried out with volatile combustibles, including mercaptans and sulfide gases. In our process the liquor is instantaneously passed through a high temperature oxidizing zone in an atmosphere strongly oxidizing, so that time and temperature are not favorable to the formation of sulfur dioxide and sulfur trioxide. Except when solid wet liquor happens to reach the fuel bed, sulfur dioxide is not formed in appreciable amount. Carbon oxysulfide is given off under our conditions, due to excess carbon dispersed in the smelt." "These temperatures are well below the boiling points of the soda salts and only sulfide and sulfate are readily volatile in air currents. It is not thought that the vapor pressures developed can lead to the dissociation of carbonates or volatilization of caustic. Sulfides will be converted to sulfates before passing out with the gases. Sulfates are readily collected."

The efficiency of the Wagner furnace in recovering

inorganic salts from the liquor fed to it is not given for the "kraft" or sulphate process. However, the efficiency is indicated as about 98% for the "soda process" in which NaOH alone is used as the active extracting agent. Since almost the same type of furnace and scrubber are used in the two processes the efficiencies may be assumed to be approximately equal.

A brief study has also been made of another type of recovery system which is outlined as follows. The liquor obtained after the extraction of organic matter from wood is first evaporated in triple or quadruple effect evaporators and then further evaporated in "disk evaporators". These contain many circular metal disks supported on a common shaft which is rotated slowly. The lower portion of each disk dips into the liquor to be evaporated and the upper portion is exposed to flue gases from the furnace. This evaporator also serves as a scrubber in removing solids and gases from the flue gases. After concentration in the disk evaporators the liquor is dried in a rotary drier by passing it countercurrent to the flue gases issuing from the furnace. Finally it is added to the furnace and burned in a reducing atmosphere so that make-up Na_2SO_4 , added to the furnace, and other inorganic sulfur compounds are reduced to Na_2S and withdrawn from the bottom of the furnace in a molten condition

together with Na_2CO_3 . These malten salts are dissolved directly in water to produce a solution which becomes the "cooking liquor" after treatment with make-up Na_2CO_3 and CaO . A certain amount of secondary air is admitted to the rotary drier through the opening through which is discharged the black ash or dried liquor. This serves as secondary air in burning combustible gases from the furnace.

This type of recovery system is not very efficient. Data obtained from a plant of the Crown Willamette Paper Co. located at Camas Wash. indicate that the liquor loses 100% of its sulfur content and 30% of its Na_2 content during each cycle.

Experimental

The problem resolved itself into finding where the large 100% loss occurred in the old type recovery system and where the small 2% loss occurred in the Wagner system. In attacking the problem it was thought to be desirable to obtain analyses of the liquors throughout the plants in order to obtain a more comprehensive idea of the process as a whole and to locate the most probable sources of loss of sulfur compounds. The step involving the loss could then be studied in detail on a small scale.

The study of a sample of dried liquor containing organic matter or "black ash" showed that the reactions of the various compounds in the system are comparatively simple. The S reacts with organic matter in the digestion process to form organic sulfur compounds, possibly mercaptans or sulfides. In the recovery furnace these organic sulfur compounds are given off as gases and more or less completely burned to SO_2 . This SO_2 is more or less completely absorbed in the scrubber system. The SO_3 and SO_4 are more or less inert in the digestion process and are reduced to S in the recovery furnace. The S_2O_3 is probably produced by reaction of S and SO_3 in solution according to the equation, $6\text{H} - 2\text{S} - 4\text{SO}_3 \rightarrow 3\text{S}_2\text{O}_3 -$

$3\text{H}_2\text{O}$. The $\text{S}_2\text{O}_3^{=}$ may or may not react with organic matter in the digestion process, but any $\text{Na}_2\text{S}_2\text{O}_3$ fed to the recovery furnace might decompose to sulfate and polysulfide⁽⁹⁾ according to the equation, $4\text{Na}_2\text{S}_2\text{O}_3 = 3\text{Na}_2\text{SO}_4 + \text{Na}_2\text{S}_5$. Thus only half of the sulfur in the $\text{S}_2\text{O}_3^{=}$ would be available for direct conversion to $\text{S}^{=}$, the remaining portion forming polysulfide sulfur which would possibly react with organic matter, be converted to SO_2 , absorbed, and converted to $\text{S}^{=}$. It was thought that polysulfide might act as a source of COS in the Wagner furnace by reacting with CO in the reducing zone. Thomas and Rule⁽¹⁰⁾ found that H_2 reacts rapidly with polysulfides at about 500 C with the formation of H_2S . Hence it was thought desirable to know the amount of $\text{S}_2\text{O}_3^{=}$ in the liquor as it entered the furnace. Also, in order to trace the reactions of $\text{S}_2\text{O}_3^{=}$ in the system, it was desirable to have a method for determining polysulfides.

Soon after the work was begun it was found that the existing systems of analysis did not give as accurate results as were required. Most of the work done so far and here reported has been in developing methods

(9) Ephraim

(10) Thomas and Rule J.C.S. 111, 1063-85

of analysis for the solids and liquids found in the system.

The most important sources of error found in the methods of analysis given by Otto Kress of the Forest Products Laboratory are as follows:

(1) In the oxidation of sulfur compounds with I_2 in basic solution part of the $S_2O_3^{2-}$ is oxidized to SO_4^{2-} , thus requiring more I_2 than for oxidation to $S_4O_6^{2-}$.

(2) It is extremely difficult to neutralize the solution containing SO_3^{2-} and $S_2O_3^{2-}$ to the methyl orange end point due to the brown coloring matter in the solution.

(3) Due to the oxidation of SO_3^{2-} by O_2 dissolved in the water an error is made in the determination of SO_3^{2-} .

The experimental data upon which these assertions are based is as follows:

(1) To a 250 cc beaker was added 10cc of standard .1 N $Na_2S_2O_3$ solution, an approximate volume of .1 N NaOH and enough water to make up to 100cc. This solution was titrated with an excess of standard I_2 solution, acidified with HCl, and back titrated to the starch end point with standard $Na_2S_2O_3$ solution.

<u>vol. 1N</u>	<u>cc I_2</u>	<u>cc $Na_2S_2O_3$</u>	<u>equiva-</u>	<u>theore-</u>	<u>% difference</u>
<u>NaOH</u>			<u>lent cc I_2</u>	<u>tical</u>	<u>from theoretical</u>
.00	9.87	.00	9.87	9.86	.00
.00	9.86	.00	9.86	9.86	.00
5	13.13	.12	13.01	9.86	31.9
5	13.07	.12	12.95	9.86	31.3
10	16.19	.07	16.12	9.86	63.5
10	16.52	.06	16.46	9.86	66.9
cc NH_4OH					
5	47.30	.56	46.75		374.

When greater concentrations of NH_4OH or NaOH are used the % error increases even further. Addition of BaCl_2 solution to these solutions after titration, produced a precipitate of BaSO_4 in the ones in which the I_2 titration had been made in basic solution, but not in the others. The amounts of the precipitates were roughly proportional to the %s difference given in the table. If all the $\text{S}_2\text{O}_3^{2-}$ were oxidized to SO_4^{2-} according to the equation, $\text{S}_2\text{O}_3^{2-} + 4\text{I}_2 + 10\text{OH}^- = 2\text{SO}_4^{2-} + 8\text{I}^- + 5\text{H}_2\text{O}$, 8 times as much I_2 would be consumed as in oxidizing the same amount of $\text{S}_2\text{O}_3^{2-}$ to $\text{S}_4\text{O}_6^{2-}$ according to the equation, $\text{S}_2\text{O}_3^{2-} + \text{I}_2 = \text{S}_4\text{O}_6^{2-} + 2\text{I}^-$. Hence the possibilities for error are large in the basic titration.

Enough C.P. Na_2SO_3 was dissolved in freshly boiled distilled water to produce an approximately .05M solution. Ten cc. of this solution was diluted to about 200cc, methyl orange added and the solution titrated to the methyl orange end point with HCl . Starch was added and the solution titrated to the starch end point with standard I_2 solution. After decolorizing with $\text{Na}_2\text{S}_2\text{O}_3$ solution the solution was again titrated to the methyl orange end point with standard NaOH solution. The SO_4^{2-} in the solution was determined by precipitating and weighing as BaSO_4 . The quantity of SO_3^{2-} taken for titration was small in order minimize possible errors due to the loss of SO_2 from the acid solution. This procedure was repeated using different conditions. Trial 1 was done as indicated above. In trial

2, 10cc of 1M NaHCO₃ was added to the solution with the Na₂SO₃ before titration in order to aid the escape of any SO₂. In trial 3 the acid produced by the reaction was not measured; the Na₂SO₃ solution was added to 200cc of solution containing equal concentrations of NH₄Ac and HAc, and the solution titrated with I₂. In trial 4 the Na₂SO₃ was added to a slight excess of I₂ solution in 200cc of water and the solution back titrated to the starch end point with standard Na₂S₂O₃ solution. In trial 5 the total sulfur content of the 10cc sample of Na₂SO₃ solution was determined by oxidizing with bromine water.

Trial	ccI ₂	ccNaOH	Equiv. NaOH Equiv. I ₂	wt BaSO ₄
1	7.75	11.80	1.500	.1229
2	7.30	11.12	1.505	.1228
3	9.50	---	---	.1230
4	9.55	---	---	.1233
5	--	---	---	.1239

The results given in this table indicate that in all the trials all of the original SO₃ was converted to SO₄, and that in the cases in which the acid produced by the reaction was measured it corresponded to the reaction HS₂O₃ and I₂ and H₂O SO₄ and 2I and 2H.

The experiment was repeated exactly except that a more concentrated Na₂SO₃ solution was used. The results are given below.

Trial	ccI ₂	ccNaOH	Equiv. NaOH Equiv. I ₂	wt BaSO ₄
1	28.84	43.90	1.501	.3877
2	27.57	41.85	1.497	.3846
3	30.53	---	---	.3900
4	30.56	---	---	.3898
5	---	---	---	.3906

The results given in this table are much the same as those given in the previous table.

In order to study the amount of acid produced by oxidation of SO_3^- by I_2 in comparison to the amount of I_2 used, another experiment was made. Trials 1 and 2 were performed as follows: A 10cc portion of Na_2SO_3 solution was added to 200cc of water and neutralized to the methyl orange end point with standard HCl . The solution was titrated to the starch end point with standard I_2 solution and to the methyl orange end point with standard NaOH solution. Trials 3 and 4 were performed as follows: The Na_2SO_3 solution was added to a solution containing almost enough I_2 for oxidation, titrated to the starch end point and then to the methyl orange end point with standard NaOH . Ratio, 1, is the ratio of equivalents of NaOH used in titrating the solution to the methyl orange end point after titrating with I_2 to the equivalents of I_2 added. Ratio, 2, is the ratio of the total number of equivalents of NaOH added to the solution to the total number of equivalents of I_2 added. The following table gives the results:

<u>Trial</u>	<u>ccI₂</u>	<u>ccHCl</u>	<u>ccNaOH</u>	<u>Ratio 1</u>	<u>Ratio 2</u>
1	24.70	12.20	37.60	1.502	.983
2	24.83	12.13	37.70	1.499	.984
3	27.27		27.64		1.001
4	27.30		27.68		1.000

These results show that the amount of acid liberated by oxidation of HSO_3^- by I_2 in acid solution, corresponding to ratio 1, is given by the equation, $\text{HSO}_3^- + \text{I}_2 + \text{H}_2\text{O} = \text{SO}_4^{2-} + 2\text{I}^- + 3\text{H}^+$. It also shows that the amount of acid produced in the oxidation of SO_3^- by I_2 , corresponding to

Equation 2, is given by the equation, $\text{SO}_3^- + \text{I}_2 + \text{H}_2\text{O} = \text{SO}_4^- + 2\text{I}^- + 2\text{H}^+$. The deviation of ratio 2 from the theoretical value 1, may be explained by loss of SO_2 .

In order to determine the effect of dissolved oxygen upon the amount of I_2 used in the reaction under various conditions, the previous experiment was repeated in part, using freshly boiled distilled water to dilute the solutions. In trials 1 and 2 the 10cc sample of Na_2SO_3 in oxygen free water was diluted to 200cc with oxygen free water, the solution titrated to the methyl orange end point with standard HCl , and then to the starch end point with standard I_2 . In trials 3 and 4 the Na_2SO_3 solution was added directly to 200cc of oxygen free water containing almost the proper amount of I_2 for oxidation, and the solution titrated to the starch end point. Conditions in the previous experiment were duplicated as closely as possible except that freshly boiled distilled water was used to dilute the solutions. The results are given in the following table.

<u>Trial</u>	<u>ccI₂</u>
1	29.33
2	29.37
3	29.85
4	29.83

These results show that the exclusion of part of the dissolved oxygen from the solutions tends to reduce the differences in the amount of I_2 used in the oxidation of Na_2SO_3 under various conditions. The effect of the complete exclusion of oxygen was not determined due to the difficulty of removing it from the I_2 solution.

From these experiments it was concluded that the oxidation of SO_3^- by I_2 in slightly acid solution is quantitative and is given by the equation, $\text{HSO}_3^- + \text{I}_2 + \text{H}_2\text{O} = \text{SO}_4^- + 2\text{I}^- + 3\text{H}^+$. The variations in the amounts of I_2 used in the oxidation of SO_3^- under different conditions cannot be explained by assuming the loss of SO_3^- as SO_2 or by assuming incomplete oxidation of the SO_3^- . The explanation suggested is the oxidation of part of the SO_3^- by O_2 dissolved in the water according to the reaction, $\text{SO}_3^- + \frac{1}{2}\text{O}_2 = \text{SO}_4^-$. In view of the fact that the oxidation of SO_3^- in basic solution or of SO_2 in acid solution by O_2 dissolved in the solution is only about 4% per hour this explanation does not seem probable. However, it is the only one which explains the facts found.

Volhard ⁽¹¹⁾ states that the anomalous results are due to the reduction of part of the sulfurous acid to sulfur by hydriodic acid according to the equation, $\text{HSO}_3^- + 3\text{H}^+ + 4\text{I}^- = 2\text{I}_2 + 2\text{H}_2\text{O} + \text{S}$. The I_2 thus produced oxidizes remaining HSO_3^- to SO_4^- according to the equation, $\text{HSO}_3^- + \text{I}_2 + \text{H}_2\text{O} = \text{SO}_4^- + 2\text{I}^- + 3\text{H}^+$. The resultant of these two equations may be written as $3\text{HSO}_3^- = 2\text{SO}_4^- + \text{S} + \text{H}_2\text{O} + \text{H}^+$. If this equation were correct the ratio equiv. $\frac{\text{NaOH}}{\text{I}_2}$, would not equal 1.5 as it actually does. Also, although a precipitate of sulfur always forms during the titration of SO_3^- with I_2 it is so extremely minute that it could not account for the large variations in the amount of I_2 used.

(11) Ann. Chem. Pharm., 242, 94

Raschig believes that the error which results when iodine is added to sulfurous acid solution is due to loss of SO_2 .

SYSTEM OF ANALYSIS

for solutions containing No Organic Matter.

Due to the fact that sulfur compounds interfere with each other in analysis, and to the fact that the solutions contain brown coloring matter which makes the use of indicators difficult it is desirable to separate as many of the constituents as possible from the solutions as solids and determine the solids.

Determination of S=

S= is separated from the solution as ZnS and titrated with standard I₂ in slightly acid solution to the starch end point. The reactions are: $ZnS + 2H^+ = Zn^{++} + H_2S$, $H_2S + I_2 = 2H^+ + 2I^- + S$, and $ZnS + I_2 = Zn^{++} + 2I^- + S$. The ZnS precipitate is transferred to a beaker, standard I₂ solution is added, and a small amount of HAc is added to hasten the solution of ZnS. After an excess of I₂ solution has been added, a small amount of HCl is poured in to complete the solution of ZnS. The excess I₂ is back-titrated with standard Na₂S₂O₃ solution. The colloidal precipitate of sulfur produced sometimes interferes with the starch end point, producing a pink color, and causing further deepening of the starch I₂ color upon standing. This effect may be removed by adding a few drops excess of standard Na₂S₂O₃ solution in the back-titration, filtering, adding starch, and titrating to the end point with standard I₂ solution. Also, the ZnS seems to be very slow in precipitating if a large excess of ammoniacal ZnCl₂ is present. This effect may be removed by using diluted ammoniacal ZnCl₂.

Procedure: To a 400cc beaker add 5cc of 1M ammoniacal $ZnCl_2$ and enough water to make up to about 150cc. Add the sample to be analyzed for $S^{=}$, and swirl the solution so as to obtain proper mixing. Allow the ZnS to settle while preparing the filter. Place a filter paper in a medium sized Hirsh funnel and after wetting it pour on a suspension of Supercel.* This forms a coating which prevents ZnS from coming in contact with the filter paper and thus makes it unnecessary to add the filter paper to the solution titrated with I_2 . Decant most of the solution containing the ZnS through the filter, mix some Supercel with the remaining solution containing the ZnS and filter. Wash the beaker and precipitate thoroughly with water. Wash the precipitate back into the beaker with water, add about 5cc of standard .1N I_2 solution, 5cc of HAc, and then I_2 solution until it ceases to disappear. Add 2cc of HCl, swirl the solution for a few seconds, and back-titrate with standard .1N $Na_2S_2O_3$ solution until a few drops of it are present in excess. Filter, add starch, and titrate to the starch end point with standard I_2 solution. If an accuracy not greater than 5% is desired the filtering may be dispensed with.

Experimental results: A solution approximately .1Min K_2S and .2N in KOH was made by dissolving H_2S in KOH solution. 10cc portions of this solution were analyzed for $S^{=}$ by the methods given above. In trials 1 and 2 no other reagents were present but in trials 3 and 4 10cc of approximately .1M Na_2SO_4 , Na_2SO_3 , $Na_2S_2O_3$, Na_2CO_3 , and NaCl were mixed

* A filter aid produced by Johns-Manville Company

with the 10cc portion of K_2S solution before determining S^{2-} in it. Also the S^{2-} in the K_2S solution was determined by precipitating with ammoniacal $AgNO_3$, filtering off the Ag_2S , dissolving it in conc. HNO_3 , and determining the Ag^+ dissolved by titrating with NH_4CNS . All the precipitates were made as nearly as possible at the same time in order to reduce errors due to the oxidation of S^{2-} . The results are given in the following tables:

Trial	cc I_2 solution	cc $Na_2S_2O_3$ solution	equiv. cc I_2 solution	equiv. I_2
1	35.46	.43	35.03	.003643
2	35.52	.45	35.07	.003648
3	35.43	.38	35.05	.003645
4	35.64	.58	35.06	.003646

$$I_2 = .1040 N$$

$$Na_2S_2O_3 = .1025 N$$

Trial	cc $AgNO_3$ solution	cc NH_4CNS solution	Equiv cc NH_4CNS	Equiv. NH_4CNS
1	.29	36.02	35.73	.003649
2	.09	35.94	35.75	.003650

$$NH_4CNS = .1021$$

$$AgNO_3 = .1025$$

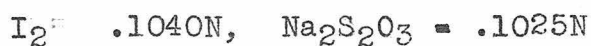
Determination of S_2^{2-}

S_2^{2-} is precipitated as ZnS_2 with ammoniacal $ZnCl_2$. In the treatment with acid and I_2 it undergoes the following reactions: $ZnS_2 + 2H^+ = Zn^{++} + H_2S + S$, $H_2S + I_2 = S + 2H^+ + 2I^-$, and $ZnS_2 + I_2 = Zn^{++} + 2S + 2I^-$. Hence, polysulfide may be calculated from the equivalents of I_2 used in oxidizing the precipitate to the starch end point and from the total sulfur in the ZnS precipitate. The equiva-

lents of I_2 gives $S^{=}$ $S_2^{=}$ and the total sulfur gives $S^{=} + 1/2S_2^{=}$. The total S in the precipitate is made by oxidation with hot acid bromine water and determination of the $SO_4^{=}$ produced by precipitating and weighing as $BaSO_4$.

Procedure: Obtain the ZnS precipitate as indicated in the previous procedure, transfer precipitate and filter paper back into the beaker in which the precipitation was made, add about 100cc of hot bromine water, then about 5cc of HCl , and boil until all the Br_2 is expelled. Filter and determine $SO_4^{=}$ in the filtrate according to the method given for $SO_4^{=}$.

Experimental results: The amount of $S_2^{=}$ found by the above method was compared with the amount found by acidifying a solution containing $S_2^{=}$ and determining the S liberated according to the reaction, $S^{=} + 2H^+ = H_2S + S$. A solution containing $S_2^{=}$ and $S^{=}$ was prepared as follows. A .1N KOH solution was saturated with H_2S , and enough sulfur added to convert about half of the $S^{=}$ to $S_2^{=}$. The solution was boiled until most of the sulfur dissolved, cooled and filtered. Enough KOH was added to produce a solution about .2N in KOH . Four 10cc portions were taken for precipitation with ammoniacal $ZnCl_2$. Two of these precipitates were titrated with I_2 , and the total sulfur in the other two determined by oxidizing with Br_2 . At the same time 2 10cc portions were acidified with HCl , the solutions allowed to stand for several minutes. The sulfur precipitates were filtered off and oxidized with Na_2O_2 . The $SO_4^{=}$ produced was determined by precipitating and weighing as $BaSO_4$. The following table gives the results:



ccI ₂	ccNa ₂ S ₂ O ₃	equiv. ccI ₂	equiv. I ₂	wt. BaSO ₄
20.78	.57	20.21	.002103	
20.86	.63	20.23	.002105	
				.4172
				.4176

$$\text{Average } m S_2^{\equiv} = .000315$$

For the direct determination of S₂[≡]

wt BaSO ₄	M S ₂ [≡]
.0730	.00313
.0735	.00315

Determination of $\text{SO}_3^{\equiv} + \text{SO}_4^{\equiv}$.

Due to the fact that SO_3^{\equiv} is oxidized to SO_4^{\equiv} in solution and during analysis and to the fact that it is difficult to separate SO_3^{\equiv} from the solutions as SO₂ without producing troublesome sulfur precipitates, SO_3^{\equiv} is oxidized to SO_4^{\equiv} with I₂ and determined with SO_4^{\equiv} . This is also more desirable in consideration of the fact that Na₂SO₄ and Na₂SO₃ undergo similar reactions upon reduction; hence their sum is more significant than either one alone. The S[≡] is separated from the solution by precipitating with ammoniacal ZnCl₂ and filtering. The SO_3^{\equiv} and $\text{S}_2\text{O}_3^{\equiv}$ in this solution are oxidized by an acid I₂ solution and the excess of I₂ back-titrated to the starch end point with standard Na₂S₂O₃ solution. The ratio of acid to oxidizing agent in the acid I₂ solution should be slightly greater than the ratio of base to reducing solution in the solution being analyzed. Upon mixing these

two solutions in any proportions I_2 is always in acid solution, being used up by the reducing solution before the solution becomes basic. The reducing solution is always basic until immediately before oxidation with I_2 , and portions of the solution which have reacted are nearly neutral so that they act merely as diluents for the remaining portion. In this way no $SO_3^{=}$ is lost due to the acidification of a solution containing much $SO_3^{=}$, yet all of the $S_2O_3^{=}$ is oxidized to $S_4O_6^{=}$ because the oxidation with I_2 is carried out in acid solution. The base in the solution may be estimated from the amount of NH_4OH added as ammoniacal $ZnCl_2$ and from the base in the sample taken; the reducing agent must be estimated by trial. After the titration SiO_2 is removed by heating and filtering, and $SO_4^{=}$ is determined by precipitating and weighing as $BaSO_4$. This method of removing SiO_2 is allowable because the amount present is extremely small. In the precipitation of $BaSO_4$, the $BaCl_2$ is added slowly thus allowing the crystals to grow slowly and to a larger size. This method is more rapid in the production of an easily filterable precipitate than the addition of a large excess of $BaCl_2$ all at once because in this case the colloidal sized crystals produced must dissolve in a solution in which they are but slightly soluble in order to recrystallize to larger ones. Addition of $BaCl_2$ at a rate slower than 1/2cc per minute of 25% solution is of no advantage because the crystals settle to the bottom and thus do not become larger. Also, in the

ignition of this crystalline precipitate it was found that subsequent treatment with concentrated H_2SO_4 does not increase the weight appreciably. Of the ten precipitates tried the gain in weight was not over .1mg, and this could be fully accounted for by the conversion of chlorides or oxides in the filter paper ash to sulfates. As in other cases colloidal sized particles have markedly different properties than larger sized particles.

Procedure: Add the sample to 5cc of 1M ammoniacal $ZnCl_2$ in 150cc of water and obtain the approximate volume of HCl required to neutralize to the methyl orange end point. Repeat the precipitation of ZnS, and filter. Transfer the filtrate to a 600cc beaker. To a 250cc beaker containing about 20% in excess of the volume of HCl required add some standard I_2 solution. Pour this solution into the one containing $SO_3^{=}$ and $S_2O_3^{=}$ and titrate to the starch end point with standard $Na_2S_2O_3$ or standard I_2 solution. Repeat until the ratio of acid to oxidizing agent is slightly greater than the ratio of base to reducing agent, and until an excess of I_2 solution is used. Record the equivalent number of cc. of I_2 solution used and use this in calculating $SO_3^{=}$ after $S_2O_3^{=}$ has been determined.

After the solution has been titrated, neutralize to the methyl orange end point, add 2cc of HCl, and heat. Filter out SiO_2 , heat to boiling, and add 25% $BaCl_2$ solution at the rate of 1/2 cc per minute for five minutes, then at the rate of 3cc per minute for fifteen minutes. Stirring action is secured by allowing the solution to boil gently.

Filter when convenient using a small Hirsh funnel and Whatman No. 4 filter paper coated with a thin layer of paper pulp. Ignite in a weighed crucible, cool, and weigh. Subtract .7mg. from the difference in weights, due to the ash in the filter paper.

Experimental: The ratio of $\text{Na}_2\text{S}_2\text{O}_3$ to I_2 obtained by titrating according to the above method was compared to the ratio obtained by titrating in neutral solution. In trials 1 and 2 the titrations were made in neutral solution. In trials 3 and 3 the $\text{Na}_2\text{S}_2\text{O}_3$ was added to 25cc of NH_4OH in 50 cc of H_2O . To this was added a slight excess of I_2 in 30cc of HCl and 50cc of H_2O . The resultant solution was titrated to the starch end point.

<u>Trial</u>	<u>ccNa₂S₂O₃</u>	<u>ccI₂</u>	<u>Ratio</u>
1	32.07	32.23	1.005
2	29.72	29.88	1.005
3	30.21	30.38	1.006
4	30.75	30.91	1.005

The volume of standard I_2 solution used in titrating a sample of Na_2SO_3 by the above method was compared with the volume used in titrating in neutral solution. Enough C.P. Na_2SO_3 was dissolved in freshly boiled distilled water to produce an approximately .05M solution. In trials 1 and 2 the Na_2SO_3 was added to an excess of standard I_2 in neutral solution and the solution back-titrated with standard $\text{Na}_2\text{S}_2\text{O}_3$ solution. In trials 3 and 4 the Na_2SO_3 was added to 25cc NH_4OH in 100cc H_2O . To this was added a slight excess of standard I_2 in 30cc HCl and 50cc H_2O . The resulting solution was titrated to the starch end point with standard $\text{Na}_2\text{S}_2\text{O}_3$ solution.

Trial	ccI ₂	ccNa ₂ S ₂ O ₃	equiv. cc I ₂
1	27.35	.42	26.93
2	27.52	.61	26.91
3	27.43	.54	26.89
4	27.60	.73	26.87

The decreasing amount of I₂ used was probably due to the oxidation of SO₃⁼ by O₂.

S₂O₃⁼ is determined by precipitating as Ag₂S₂O₃ in nitric acid solution after the S⁼ has been removed with ammoniacal Zn(NO₃)₂, and allowing the precipitate to decompose according to the equation, Ag₂S₂O₃ + H₂O = Ag₂S + H₂SO₄. The nitric acid catalyzes the decomposition and causes it to be complete within one minute. Enough NH₄OH is then added to dissolve other silver salts which may have precipitated, and the Ag₂S is filtered off. The Ag₂S is determined by oxidizing in concentrated HNO₃ and titrating with standard NH₄CNS.

A large concentration of SO₃⁼ in the solution containing the S₂O₃⁼ sometimes introduces an error due to precipitation of Ag₂SO₃ and its inclusion by the Ag₂S₂O₃ precipitate. However, this error may be removed by precipitating under conditions which produce no precipitate of Ag₂SO₃, that is in strongly acid solution. Decomposition of S₂O₃⁼ by the acid is prevented by adding acid and AgNO₃ together. Inclusion of AgCl by the Ag₂S₂O₃ precipitate introduces no error because the AgCl is not dissolved upon treating with HNO₃.

Procedure: Add the sample to 5cc 1M ammoniacal Zn(NO₃)₂ in 150cc H₂O, and filter. Transfer the filtrate

Determination of Na_2

Na_2 is determined by converting the inorganic salts to NaCl , NaBr , and Na_2SO_4 , and determining each. The inorganic sulfur compounds are oxidized to SO_4^{2-} by acid Br_2 water and the remaining inorganic salts are converted to bromides by acidifying with HBr and evaporating to dryness. The salts are dissolved and the solution diluted to a definite volume. A portion is taken for the determination of Cl^- and Br^- by titrating with standard AgNO_3 solution until an excess is present, filtering, and back titrating with NH_4CNS using ferric alum as an indicator. Also, a portion is taken for the determination of SO_4^{2-} . Bromides are used instead of chlorides because they are more easily determined with AgNO_3 . As AgNO_3 is added with stirring to a hot solution containing Br^- , coagulation of the precipitate takes place very rapidly as soon as a few drops of AgNO_3 solution are present in excess. The solution may be filtered immediately without danger of losing AgNO_3 , and back-titrated with standard NH_4CNS solution.

Procedure: Add the sample to an excess of Br_2 water, acidify with HBr and evaporate to dryness. Heat with a smoky flame until all of the HBr has been driven off. Cool, dissolve in H_2O and filter. Add to a volumetric flask and dilute to the mark. Pipet a portion into a beaker, heat to boiling and titrate with standard AgNO_3 solution until the precipitate begins to coagulate rapidly. Filter and back-titrate with standard NH_4CNS solution using ferric alum as an indicator.

SYSTEM OF ANALYSIS

For Liquor Containing Organic Matter

Due to the black color of these solutions colored indicators cannot be used to determine end points; the constituents must be separated from the solution as solids or gases. Upon acidifying most of the organic matter is precipitated as a jelly like precipitate which is very difficult to handle. A 3 gram sample of the dried liquor containing about enough $\text{SO}_4^{=}$ + $\text{SO}_3^{=}$ to produce a .3 gram precipitate of BaSO_4 produces about 30cc of a jelly like precipitate upon dissolving and acidifying. A vacuum cannot be used as an aid to filtering if the filtrate is desired because of the foaming properties of the solution, a few cc. of the liquor being sufficient to fill even the largest filtering flask with foam. In some cases the presence of rosin in the solution also increases the difficulty of filtering.

It has been found that filtering may be done easily if about 50# / sq. in. pressure is used and the precipitate is suspended in a large volume of Supercel to prevent its clogging the filter paper. An airtight container was made for a medium sized Buchner funnel, having an opening for the stem of the funnel and a lid which could be taken off and put on easily.

Upon acidifying and filtering the black solution a clear light brown solution is obtained which may be titrated with I_2 solution to the starch end point. However, since

I_2 oxidizes mercaptans to sulfides and sometimes forms addition compounds with sulfides, ⁽⁹⁾ and since SO_3^- may be oxidized by dissolved O_2 during the determination, this titration is not used in determining any of the constituents. Even if it were accurate it would be of no value unless a separate determination could be made of $S_2O_3^-$ or SO_3^- .

The method of analyzing for thiosulfate by precipitating with $AgNO_3$ in acid solution is interfered with by the presence of some organic compound. If S^- is removed by precipitating with ammoniacal $Zn(NO_3)_2$ and filtering, the solution acidified with HNO_3 and the organic matter filtered off a clear brown solution is obtained. Addition of $AgNO_3$ produces a white precipitate which rapidly becomes black as in the case of $S_2O_3^-$. However, upon the addition of an excess of NH_4OH a colloidal precipitate is produced which is almost impossible to filter. Such a precipitate is not produced when $S_2O_3^-$ alone is present.

Determination of S^-

S^- is determined in exactly the same way as given for a solution containing no organic matter.

Determination of SO_4^- SO_3^- .

SO_4^- SO_3^- is determined in the same way as given for a solution containing no organic matter except that the I_2 titration is not taken and the precipitate of organic matter obtained upon acidifying is filtered off before the determination of SO_4^- .

The main sources of error in the determination of $\text{SO}_4^{=}$ are the precipitation of other barium salts than BaSO_4 and the occlusion of organic matter by BaSO_4 . If the determination of BaSO_4 is made in the usual way an almost black precipitate is obtained upon ignition, and discrepancies are often as high as 20%. The black color of this precipitate is not removed by treatment with H_2SO_4 or with O_2 at red heat. However, if the precipitate is heated to a high temperature in an oxidizing flame on a platinum foil it suddenly loses its blackness and at the same time the flame assumes the green barium color. Like other organic barium salts this salt seems to be much more soluble in acid solution and at high temperatures. Its precipitation may be prevented by precipitating and filtering the BaSO_4 hot and in a solution of correct acidity. Occlusion of organic matter by BaSO_4 is reduced by the formation of larger crystals of BaSO_4 .

Procedure: Add the sample to 5cc of 1M ammoniacal ZnCl_2 in 150cc H_2O . Filter with pressure into a 600cc beaker and wash the precipitate and beaker thoroughly with water. Acidify with acetic acid, add 100cc of Supercel, and filter with pressure. Titrate with I_2 to the starch end point. Repeat the precipitation and filtration of ZnS . To the filtrate add a solution containing about 20% excess I_2 solution and 30% HCl to react with the reducing agent and base. Heat to about 40-50°C and allow the precipitate to coagulate. Filter, using pressure, and wash the precipitate thoroughly with very dilute HCl . Neutralize

to the methyl orange end point, add 2cc of HCl and determine $\text{SO}_4^{=}$, filtering the solution while still hot.

Determination of total sulfur.

The total sulfur content of the liquor is determined by oxidizing with Br_2 for several hours, filtering off the precipitate, and oxidizing it with Na_2O_2 . All the $\text{SO}_4^{=}$ is added together and determined by precipitating and weighing as BaSO_4 . The liquid bromine reacts rapidly with the organic matter producing a well coagulated rust colored precipitate which may be filtered easily. Inorganic sulfur compounds are oxidized by Br_2 to $\text{SO}_4^{=}$. Also mercaptans and organic sulfides are slowly oxidized to sulfates.

Procedure: To the sample in a 250cc flask add about 1cc Br_2 and cover with a watch glass. Allow to react for about 3 hours. Dilute to 100cc and filter, using a small Hirsh funnel. Transfer the precipitate to a nickel crucible add Na_2O_2 and heat. As soon as the fusion is complete pour most of the molten salt on to a sheet of nickel and allow to cool. Set the crucible in a 600cc beaker, dissolve the salts with dilute HCl, and wash the crucible with water. Add the main portion of salt from the sheet of nickel and dissolve by acidifying. Filter into the filtrate previously obtained and return the total filtrate to the beaker. Determine $\text{SO}_4^{=}$.

Determination of Na_2 .

The determination of Na_2 is carried out in the same way as given for solutions containing no organic matter.

Sample calculation of an analysis:

The following data sheet gives a brief outline of the calculations involved in the analysis of a cooking liquor obtained from a plant of the Crown Willamette Paper Co. located at Port Townsend, Washington.

$S^=$ and $S_2^=$ were precipitated with ammoniacal $ZnCl_2$ from four 5cc portions of liquor. Two of the precipitates were titrated with I_2 , and two were oxidized with hot Br_2 water and $SO_4^=$ determined.

<u>ccNa₂S₂O₂</u>	<u>ccI₂</u>	<u>equiv. cc I₂</u>	<u>wt BaSO</u>
1.17	25.29	24.61	.2957
1.59	26.26	<u>24.65</u>	<u>.2959</u>
average		24.63	.2958

$$I_2 = .1021N$$

$$Na_2S_2O_3 = .1030N$$

$$\text{mols } S^= + \text{mols } S_2^= = \frac{\text{equiv. } I_2}{2} = \frac{(.02463)(.1021)}{2} = .001258$$

$$\text{mols } S^= + 2 \text{ mols } S_2^= = \text{mols } BaSO_4 = \frac{.2958}{233.4} = .001267$$

$$\text{mols } S_2^=/\text{liter} = (.001267 - .001258) \frac{1000\text{cc}/\text{liter}}{5\text{cc in sample}} = .0002$$

$$\text{mols } S^=/\text{liter} = \frac{(.00258)}{5} = .0002 = .2498$$

$S^=$ and $S_2^=$ were precipitated and filtered from two 10cc portions of liquor, the filtrates oxidized with acid I_2 and $SO_4^=$ determined in the solution

<u>ccNa₂S₂O₃</u>	<u>ccI₂</u>	<u>equiv. cc I₂</u>	<u>wt BaSO₄</u>
.85	7.55	6.69	.3849
.05	6.75	<u>6.70</u>	<u>.3852</u>
Average		6.69	.3850

$$\begin{aligned}
 (2 \text{ mols } \text{SO}_3^{=} + \text{M } \text{S}_2\text{O}_3^{=}) \text{ per liter} &= (\text{equiv. I}_2) \frac{1000 \text{ cc per liter}}{10 \text{ cc in sample}} \\
 &= \frac{(6.69)(.1021)}{10} = .0673
 \end{aligned}$$

$$\begin{aligned}
 (\text{mols } \text{SO}_3^{=} + \text{mols } \text{SO}_4^{=}) \text{ per liter} &= \text{mols BaSO}_4 \frac{1000 \text{ cc per liter}}{10 \text{ cc in sample}} \\
 &= \frac{3850 (1000)}{233.4 \cdot 10} = .1650
 \end{aligned}$$

S⁼ and S₂⁼ were precipitated and filtered from two 25cc portions of solution with ammoniacal Zn(NO₃)₂, the solutions acidified with HNO₃ and acid AgNO₃ added. NH₄OH was added, and the Ag₂S determined.

<u>cc AgNO₃</u>	<u>cc NH₄CNS</u>	<u>equiv. cc NH₄CNS</u>
.00	18.43	18.43
.06	18.51	18.45
		<u>18.44 = Average</u>

$$\text{NH}_4\text{CNS} = .1021$$

$$\begin{aligned}
 \text{mols } \text{S}_2\text{O}_3^{=} \text{ per liter} &= \frac{(\text{equiv. NH}_4\text{CNS})}{2} \frac{1000 \text{ cc per Liter}}{25 \text{ cc in sample}} \\
 &= \frac{(18.44)}{2} \frac{(.1021)}{25} = .03763
 \end{aligned}$$

$$\text{M } \text{SO}_3^{=} \text{ per liter} = \frac{(.0673 - .0376)}{2} = .0148$$

The total S in two 5cc samples was determined by oxidizing with Br₂ water and determining SO₄⁼.

wt BaSO ₄
.5578
<u>.5574</u>
Aver. .5576

$$\begin{aligned}
 \text{mols S/liter} &= (\text{mols BaSO}_4) \frac{1000 \text{ cc per liter}}{5 \text{ cc in sample}} \\
 &= \frac{.5576 (1000)}{233.4 \cdot 5} = .4775
 \end{aligned}$$

Two 5cc samples were treated with Br_2 water and then with HBr and evaporated to dryness. Cl^- and Br^- were determined by titrating with AgNO_3 and NH_4CNS

<u>ccAgNO₃</u>	<u>ccNH₄CNS</u>	<u>equiv. ccAgNO₃</u>
150.45	11.48	139.25
144.91	15.34	139.70
		<u>139.4 = Average</u>

AgNO_3 - .1025N
 NH_4CNS - .1021N

$$\begin{aligned} (\text{mols } \text{Br}^- \text{ and } \text{Cl}^-) \text{ per liter} &= (\text{m } \text{AgNO}_3) \frac{1000 \text{ cc per liter}}{5 \text{ cc in sample}} \\ &= \frac{(139.4)}{5} \cdot 1025 \\ &= 2856 \end{aligned}$$

$$\begin{aligned} \text{m Na}_2 \text{ per liter} &= (\text{m } \text{SO}_4^{2-} + 1/2\text{m}(\text{Br}^- + \text{Cl}^-)) \text{ per liter} \\ &= .4775 + \frac{2.856}{2} = 1.905 \end{aligned}$$

	<u>m/liter</u>	<u>m/m Na₂</u>
S_2^{2-}	.0002	.0001
S^{2-}	.2498	.1310
$\text{S}_2\text{O}_3^{2-}$.0376	.0198
SO_3^{2-}	.0148	.0078
SO_4^{2-}	.1502	.0789
Total S^{2-}	.4775	.2510
$2 \text{S}_2^{2-} + \text{S}^{2-} + 2\text{S}_2\text{O}_3^{2-} + \text{SO}_3^{2-} + \text{SO}_4^{2-}$	= .4904	m/liter
Total S	= .4775	m/liter

$$\% \text{ difference} = \frac{(.4904 - .4775)}{.4775} 100 = 2.7\%$$

Analysis of Liquors from Plant Using Wagner Furnace

The methods previously outlined were used in analyzing liquors obtained from a plant of the Crown Willamette Paper Co., located at Port Townsend, Wash. This plant uses a Wagner furnace. The samples of liquor were collected at about the same time so as to be comparable to one another. The liquors are as follows:

- I Scrubber liquor
- II Liquor entering digestors
- III Liquor leaving digestors
- IV Concentrated liquor entering furnace
- V Concentrated liquor after decomposing at about 500°C, in the laboratory.

The data are given in mols per mol of Na₂ so that the different analyses are comparable. The analyses are as follows:

	I	II	III	IV	V
S ₂ ⁼	.0000	.0001	.0000	.0000	.0000
S ⁼	.1115	.4310	.0001	.0000	.0000
S ₂ O ₃ ⁼	.0351	.0198	---	---	.0000
SO ₃ ⁼	.1008	.0078	---	---	.0048
SO ₃ + SO ₄ ⁼	.1565	.0789	.0865	.0477	.0745
Total S	.3315	.2510	.2481	.2354	.0745
mols Na ₂ /liter	.5339	1.905	.8045	***	****

Discussion of results:

The analyses of the scrubber liquor and liquor entering digestors probably do not represent their composition at the time the samples were taken with an accuracy less than 5%. However, the analyses of the liquors containing organic matter probably represent their composition at the time the samples were taken with an accuracy of less than 1% due to the absence of S⁼.

The inorganic sulfur compounds in the liquor entering the digestors are $S^{=}$, $S_2O_3^{=}$, SO_3 , and $SO_4^{=}$. Their general reactions in the system are as follows:

All of the $S^{=}$ in the original cooking liquor reacts with organic matter in the digestion process to form organic sulfur compounds. Upon drying and heating the liquor to $500^{\circ}C$, a temperature below the temperature of reduction of Na_2SO_4 by C, these organic sulfur compounds are given off as gases and liquids, their odor suggesting mercaptans or sulfides. In the furnace these organic sulfur compounds are burned to SO_2 , and are absorbed in the scrubber. The scrubber liquor is therefore the main source of inorganic sulfur compounds capable of being reduced to $S^{=}$ in the furnace.

The reactions of $S_2O_3^{=}$ are unknown. Although $Na_2S_2O_3$ decomposes upon heating to about $300^{\circ}C$ according to the equation $4 Na_2S_2O_3 = 3 Na_2SO_4 + Na_2S_5$, the fact that no $S^{=}$ or $S_x^{=}$ was found in the liquor after drying and heating to $500^{\circ}C$ does not indicate that no $S_2O_3^{=}$ was present in the liquor before heating because the $S_x^{=}$ produced may have reacted with organic matter to form volatile organic sulfur compounds.

The $SO_4^{=}$ and $SO_3^{=}$ are comparatively next in the digestion process and are reduced to $S^{=}$ in the furnace.

Although the ratio of volume of scrubber liquor taken from scrubber to volume of liquor entering digestors per unit time is not known it is assumed that this ratio is approximately one. The reasons for this assumption are as

follows: The sulfur content of the scrubber liquor withdrawn from the scrubber per unit time should be at least half of the sulfur content of the liquor entering the digestors per unit time because the $S^{=}$ in the latter is converted to organic sulfur compounds, burned to SO_2 and absorbed in the scrubber. The scrubber liquor contains $S^{=}$ available for use in the digesting process; therefore the scrubber liquor is added to the cooking liquor before entering the digestors instead of after leaving. Also, if the scrubber liquor were added to the cooking liquor as it left the digestors additional evaporation would be necessary to concentrate the liquor. It is desirable to maintain the concentration of $S^{=}$ in the scrubber liquor as low as possible in order to minimize losses of H_2S ; therefore water is added to the system in the scrubber. The scrubber liquor is then used to dissolve the molten salts from the furnace to produce the cooking liquor or liquor entering digestors. However, water is added to the cooking liquor in washing the precipitate of $CaCO_3$ obtained upon causticizing with CaO .

The comparatively large amounts of Na_2 and $S^{=}$ in the scrubber liquor cannot be explained by vaporization of inorganic salts in the furnace. The explanation offered is the entrainment of liquor sprayed into the furnace in the gases passing to the scrubber. The facts upon which this view is based are as follows: The scrubber liquor contains finely divided carbon particles amounting to about 5% of

its volume. Also, the liquor entering the furnace upon heating forms a porous mass of about 5 times the volume of the liquor, as does sugar. The explanation offered for the S^- on the scrubber liquor is the reduction of Na_2SO_4 by C in the entrained particles carried to the scrubber. The facts upon which this view is based are the rapidity of the reduction of Na_2SO_4 by C and the high temperature to which the particles are exposed. It is thought that subsequent oxidation of Na_2S to Na_2SO_4 by O_2 is slower than the oxidation of C by O_2 . Carbon is present in the scrubber liquor. Also, the fact that gases from the furnace are cooled down quickly upon passing through a boiler would decrease the oxidation of Na_2S to Na_2SO_4 .

Discussion of possible losses of sulfur compounds.

Losses of chemicals from the system can take place only in the rejected wash water used in washing the pulp and in the flue gases passing from the scrubber. It is assumed that the former is the smaller loss. The ratio of S to Na_2 in the rejected wash water is as given by the analysis of the liquor leaving the digestors. The ratio of Na_2SO_4 to Na_2CO_3 added to the system is about 1/10, corresponding to a value of .931 for the ratio of S to Na_2 . The ratio of S to Na_2 in the solids in the flue gases is about as given by the analysis of the liquor after decomposing at about $500^\circ C$. Consequently, the main loss of sulfur compounds is the loss of gaseous sulfur compounds in the flue gas passing from the scrubber.

The most probable losses of gaseous sulfur compounds are the loss of H_2S due to hydrolysis of $S^=$ in the scrubber liquor, loss of unburned organic sulfur compounds, and loss of SO_2 due to incomplete absorption in the scrubber. Experiments on the combustion of the organic matter given off upon heating have met with complete failure possibly because the combustions were performed at only 700° - $800^{\circ}C$ and because enough time was not allowed for combustion. These sulfur compounds are given off as colloidal sized liquid particles which are almost impossible to absorb and which burn incompletely at 700° - $800^{\circ}C$ to give colloidal smoke particles. Further experiments will be made to determine the rate of combustion at about $1000^{\circ}C$ to $1100^{\circ}C$, the temperatures employed in the Wagner furnace.

Improvements in the recovery of sulfur compounds should be directed toward the removal of Na_2S from the scrubber, more complete combustion of organic matter, and more complete absorption of SO_2 in the scrubber. Removal of Na_2S could be accomplished by the removal of solids from the flue gases before passing to the scrubber using a Cohrell precipitator or bag filters. It would not be desirable to remove all of the solids from the flue gases before passing to the scrubber because Na_2CO_3 in the scrubber liquor helps in the absorption of SO_2 . More complete combustion of organic sulfur compounds could be secured by allowing a longer time for combustion by increasing the length of the combustion zone. More complete absorption of SO_2 from the flue gases could be accomplished by changing the design of the scrubber.

It has been found that it is undesirable to add the double salt of Na_2SO_4 and Na_2CO_3 , burkeite, to the furnace in the usual way by blowing it in with air because this salt is so fine that a great deal of it is carried into the scrubber by the flue gases. This is undesirable because in the evaporation of the resultant liquor Na_2SO_4 is more liable to precipitate on the evaporator tubes. The alternative point of addition is to the concentrated liquor entering the furnace. Wagner states that addition of Na_2SO_4 to this liquor causes solid precipitation with consequent clogging of the spraying nozzles. Experiments showed that the addition of Na_2SO_4 or Burkeite introduced no solid other than the one added. However, the effect of this solid upon the spraying nozzle was not determined. However, the chemical effects of addition of Na_2SO_4 or burkeite to the liquor can be predicted. A large proportion of the Na_2SO_4 would pass into the scrubber, either as Na_2SO_4 or Na_2S by entrainment of the liquor in the flue gases. Either condition would be undesirable. If Na_2S were produced due to the reduction of Na_2SO_4 by C the losses of S^- from the scrubber due to hydrolysis would increase. This would reduce the ratio of Burkeite to Na_2SO_4 added to the system. If the Na_2SO_4 were not reduced it would increase the liability of precipitation of Na_2SO_4 during evaporation.

Analysis of Black Ash From Plant Not Using Wagner Furnace:

The methods previously outlined were used in analyzing a sample of black ash from a plant of the Crown Wilamette

Paper Co., located at Camas, Wash. This plant uses the system of recovery outlined in the introduction to this paper. The black ash is liquor containing organic matter which has been dried in a rotary kiln by flue gases from the reduction furnace at a fairly low temperature. The analyses are as follows, the data being given in mols per mol of Na_2

I Black Ash

II Black Ash after decomposing at about 500°C in the laboratory.

	I	II
S=	.000	.0000
SO_3 =	---	.0742
SO_4 SO_3	.1226	.1290
Total S	.2681	.1290

From these analyses and from the difficulty of burning the organic sulfur compounds given off it was concluded that the large loss of sulfur compounds in this plant was due to incomplete combustion of organic sulfur compounds and absorption as SO_2 .

Since any improvement in this recovery system would mean a radical change in the design of the furnace it was thought advisable to discontinue work on this system.

In order to make up for the large ratio of S to Na_2 lost from the system this plant increases the ratio of S to Na_2 added by adding NaHSO_4 with the Na_2SO_4 . This NaHSO_4 is becoming increasingly difficult to obtain. A purely chemical means of making the addition of NaHSO_4 to the system unnecessary was devised which depends upon the separation of Na_2CO_3 from the system. This method is given

as follows: The molten salts from the reducing furnace containing mostly Na_2CO_3 and Na_2S are dissolved in just enough water to form a saturated solution of $\text{Na}_2\text{S} \cdot 9 \text{H}_2\text{O}$. Under these conditions excess Na_2CO_3 precipitates as $\text{Na}_2\text{CO}_3 \cdot 10 \text{H}_2\text{O}$. This precipitate may be removed from the system by filtering and washing.

In order to determine whether or not this system would work the solubility was roughly determined of $\text{Na}_2\text{S} \cdot 9\text{H}_2\text{O}$ and $\text{Na}_2\text{CO}_3 \cdot 10 \text{H}_2\text{O}$ in a solution saturated with each. Enough C.P. Na_2S and Na_2CO_3 were dissolved in hot distilled water to correspond to the solubilities of $\text{Na}_2\text{S} \cdot 9 \text{H}_2\text{O}$ and $\text{Na}_2\text{CO}_3 \cdot 10 \text{H}_2\text{O}$ in water. The solution was cooled, seeded with $\text{Na}_2\text{S} \cdot 9\text{H}_2\text{O}$ and $\text{Na}_2\text{CO}_3 \cdot 10 \text{H}_2\text{O}$, and kept in a thermostat at 25°C for 3 days. The solution was allowed to settle, a portion was pipetted off and diluted to a definite volume. $\text{S}^{=}$ was determined by precipitating and weighing as Ag_2S , and $\text{S}^{=} \text{CO}_3^{=}$ were determined by titration to the methyl orange end point with standard HCl . The results are given as follows:

Solubility of $\text{Na}_2\text{S} \cdot 9\text{H}_2\text{O}$ in g. $\text{Na}_2\text{S}/100 \text{ g. H}_2\text{O} = 8.15$

Solubility of $\text{Na}_2\text{CO}_3 \cdot 10 \text{H}_2\text{O}$ in g. $\text{Na}_2\text{CO}_3/100 \text{ g H}_2\text{O} = 20.3$

Ratio of $\text{S}^{=}$ to $\text{Na}_2 = .353$

The solubilities in water are as follows:

Solubility of $\text{Na}_2\text{S} \cdot 9 \text{H}_2\text{O}$ in g. $\text{Na}_2\text{S}/100 \text{ g. H}_2\text{O} = 17.1$

Solubility of $\text{Na}_2\text{CO}_3 \cdot 10 \text{H}_2\text{O}$ in g. $\text{Na}_2\text{CO}_3/100 \text{ g. H}_2\text{O} = 29.6$

Since the ratio of total S to Na_2 used at the plant at Port Townsend is only .251 this method of separating Na_2CO_3 from the system is theoretically possible.

SUMMARY

A system of analysis has been developed for the inorganic constituents, $S_2^=$, $S^=$, $S_2O_3^=$, $SO_3^=$, and $SO_4^=$ as well as total sulfur in the liquors used in the manufacture of paper pulp by the kraft process.

This system of analysis has been used in analyzing samples of liquor obtained from a paper pulp plant using a Wagner furnace in order to determine the most probable sources of loss of sulfur compounds from the system.

The losses of sulfur compounds from the system have been found to occur mainly in the flue gases from the scrubber system. The possible sulfur compounds lost were found to be H_2S , SO_2 , and organic sulfur compounds.

Methods of increasing the efficiency of recovery of sulfur compounds have been suggested.

A possible method for the removal of Na_2CO_3 from the system has been discovered.

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