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Radiochemical Determination of Polythionates

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Two radiochemical methods have been developed for the determination of polythionates. In the first method, the polythionates are reacted with sulphite and with a mixture of sulphite and sulphide. The thiosulphate formed in these reactions is then determined with ^{110}AgSCN. In the second method, the sulphide contains the radioactive isotope ^{35}S and the amount of radioactive thiosulphate formed is instead determined. A correction must be applied for the amount of radioactive thiosulphate formed by isotopic exchange between the sulphide and thiosulphate.

The common method for determining polythionates in mixtures is based on the fact that these ions, on reaction with sulphite, sulphide, cyanide, and hydroxide, give amongst other compounds thiosulphate [1,2]. The thiosulphate formed can be determined iodometrically in a weakly acid solution after the disturbing influence of sulphite, sulphide and cyanide has been eliminated.

In the present work, two radiochemical methods for the determination of the total amount of polythionate have been developed. Both of the methods are intended for use in the determination of polythionate in spent liquors from the sulphite cellulose process. With the iodometric method, the errors are considerable in this case and with many types of liquors it is impossible to use a method of this sort.

In the first method, the amount of thiosulphate formed in the reaction with sulphite and the amount of thiosulphate formed in the reaction with a mixture of sulphite and sulphide are determined. The thiosulphate determinations are performed by means of the silver thiocyanate method using silver thiocyanate containing the radioactive isotope ^{110}Ag. From these two determinations, it is possible to calculate the amount of polythionate as well as the mean number of sulphur atoms per mole polythionate.

In the second method, the polythionates are first made to react with sulphite and then with sulphide containing the radioactive isotope ^{35}S. After precipitation of sulphide, the amount of radioactive thiosulphate formed is determined. From this determination, it is possible to calculate the original amount of polythionate after correcting for the radioactive thiosulphate which is formed by isotope exchange between thiosulphate and sulphide.

I. THE SILVER(^{110}Ag) THIOCYANATE METHOD

Polythionates with more than three sulphur atoms per molecule react in alkaline solution with sulphite forming thiosulphate and trithionate according to the equation:

$$S_nO_6^{2-} + (n-3)\ SO_3^{2-} \rightarrow S_3O_6^{2-} + (n-3)\ S_2O_3^{2-},\ n > 3 \qquad (1)$$

Even at room temperature, the reaction proceeds very rapidly in the presence of an excess of sulphite. Trithionate does not react with sulphite under the conditions existing in this case. In weakly acid or neutral solutions, the reaction proceeds slowly. Moreover, the reaction does not give a complete yield, a state of equilibrium being instead obtained.

In the reaction between polythionates and a mixture of sulphite and sulphide, it has been found that all of the polythionates give thiosulphate according to the equation:

$$S_nO_6^{2-} + S^{2-} + (n-3)\ SO_3^{2-} \rightarrow (n-1)\ S_2O_3^{2-},\ n \geq 3 \qquad (2)$$

This reaction is carried out at about 100°C since the reaction rate is relatively low at room temperature.

If the amount of thiosulphate formed in these two reactions is determined, it is possible to calculate the total amount of polythionate in the following way:

In a solution containing a_2 mole $S_2O_3^{2-}$, a_3 mole $S_3O_6^{2-}$, a_4 mole $S_4O_6^{2-}$, ... a_n mole $S_nO_6^{2-}$, we obtain after the reaction with sulphite a thiosulphate amount, $A = a_2 + \Sigma(n-3)\ a_n$, and after the reaction with sulphite-sulphide a thiosulphate amount, $B = a_2 + \Sigma(n-1)\ a_n$. From these two quantities, the amount of polythionate is obtained as $\Sigma a_n = \frac{B-A}{2}$ while the average number of sulphur atoms per molecule is

$$\bar{n} = \frac{n\Sigma a_n}{\Sigma a_n} = \frac{B + \frac{B-A}{2} - a_2}{\frac{B-A}{2}}$$

In order to calculate $\bar{n}$, it is evident that the original thiosulphate content of the solution must be determined. As has been previously shown [3], it is also possible to perform this determination with the silver thiocyanate method.

The determination of thiosulphate with the silver thiocyanate method is based on the property of the thiosulphate ion of forming stable silver thiosulphate complexes with silver ions [4]. Thus, if an excess of solid silver thiocyanate is shaken with a thiosulphate solution, the following equilibrium between the solid phase and solution is obtained after only 10 min at 20°C:

$$m\ AgSCN_{(s)} + n\ S_2O_3^{2-} \rightleftharpoons Ag_m(S_2O_3)_n^{(2n-m)-} + m\ SCN^-$$

Since the silver thiocyanate contains the radioactive isotope ^{110}Ag, the total amount of silver in the solution can be determined by measuring the activity of the solution after removal of the solid phase. The thiosulphate content is then calculated by means of a calibration curve between thiosulphate content and silver content.

The determination of the thiosulphate which is formed in the sulphite reaction is complicated by the fact that the sulphite ions like the thiosulphate ions give stable complexes with silver ions. The formation of silver sulphite complexes can, however, be completely avoided if the solution is acidified before the analysis. This is due to the fact that hydrogen sulphite ions in contrast to sulphite ions do not form complexes with silver ions. However, it has been found [3] that hydrogen sulphite has a certain effect on the determination of thiosulphate by the silver thiocyanate method. In the present work, it has therefore been necessary to study how this effect depends on the pH of the solution, in order to determine to what pH the solution should be adjusted after the sulphite reaction.

Before determining the thiosulphate after the sulphite-sulphide reaction, the remaining sulphide is removed by precipitation with zinc carbonate. The solution is thereafter acidified in order to convert the sulphite to hydrogen sulphite. The effect on the thiosulphate determination of any possible remaining traces of sulphide was also studied.

Experimental

Chemicals

Potassium trithionate, $K_2S_3O_6$, has been prepared according to Kurtenacker and Matejka [5] and potassium pentathionate, $K_2S_5O_6 \cdot 1.5\ H_2O$, according to Stamm, Siepold and Goehring [6]. Sodium tetrathionate, $Na_2S_4O_6 \cdot 2\ H_2O$, was prepared by shaking solid sodium thiosulphate with an excess of iodine dissolved in absolute alcohol. The purity of the trithionate and pentathionate was better than 97 % while the impurity content in the tetrathionate was less than 0.5 %. The purity of these substances was determined using the sulphite method and the sulphite-sulphide method as described by Kurtenacker [1] and using the mercury(II) chloride method according to Jay [7].

The sodium sulphide solution was prepared by passing hydrogen sulphide into a sodium hydroxide solution. The surface of the sulphide solution was covered with paraffin oil in order to minimize aerial oxidation. The sulphite solution was freshly prepared for each series of experiments.

The silver isotope, ^{110}Ag, was provided by AB Atomenergi — it had been prepared by neutron irradiation of a piece of silver foil. About 1 g of foil was irradiated to an activity of 1—2 mC. It was then dissolved in 50 ml hot nitric acid (diluted 1:4) and diluted to 500 ml. Of this solution, 100 ml was taken and sufficient inactive silver nitrate added to lower the activity to 800—1 000 c.p.m./10^{-4} M silver (GM-tube for liquids). The solution obtained was diluted and silver thiocyanate was precipitated at about 100°C using an excess of potassium thiocyanate solution. The precipitate was washed with water until the washings no longer produced a colour with iron(III) nitrate. In order to determine the relation between activity and silver content, a weighed amount of silver thiocyanate was dissolved in an excess of 1 M potassium cyanide. After diluting, 10 ml of the solution was taken for activity measurements.

Apparatus

The shaking of the silver thiocyanate suspension was carried out using a "Microid flask shaker" from Griffin and George Ltd. The filtering of the suspension was performed in a Thiessen filtration apparatus provided with a colloid filter (according to Zsigmondy). The pore width of the colloid filter was 200—300 mμ.

The radioactivity was measured with a GM-tube for liquids made by Mullard Ltd. Before each measurement, the GM-tube had to be washed with conc. potassium cyanide solution. The scaler used was a Type 1 000 apparatus from AB Nukleonikinstrument, Göteborg.

Procedure

The sulphite reaction. To 10 ml of the sample, 5 ml 0.4 M sodium sulphite was added after which the solution was allowed to stand for 15 min at room temperature. The solution was acidified with 5 ml 0.5 M formic acid and, to 10 ml of the solution thus obtained, 10 ml silver thiocyanate suspension containing 10—25 mg precipitate was added. The mixture was shaken vigorously for 15 min at 20 ± 1°C after which the solution was filtered. The activity was measured on 10 ml of the filtrate. The activity obtained was corrected for background radiation and radioactive decay.

The sulphite-sulphide reaction. To 25 ml of the sample, 5 ml 0.4 M sodium sulphite and 5 ml 0.25 M sodium sulphide were added and the solution was heated in boiling water for 15 min. Then, 10 ml 0.35 M freshly prepared zinc carbonate suspension was added and the mixture was cooled to room temperature and filtered. After adding 10 ml 1 M formic acid, the filtrate was diluted to 100 ml. A 10 ml sample of this solution was taken and 10 ml silver thiocyanate suspension was added. Shaking and filtration were performed as described above.

Results

Determinations of the thiosulphate formed in the sulphite and sulphite-sulphide reactions are shown in Table 1. In order to be able to compare the

Table 1. Determination of polythionates using the silver(^{110}Ag)thiocyanate method.

Reaction	Polythionate, added			$c_{S_2O_3} \times 10^3$ Calc.	$c_{Ag} \times 10^3$		Deviation %
	$cS_3O_6 \times 10^3$	$cS_4O_6 \times 10^3$	$cS_5O_6 \times 10^3$		Found	Calc.	
sulphite		0.05		0.05	0.036	0.036	0.0
		0.1		0.1	0.068	0.067	+ 1.5
		0.3		0.3	0.181	0.186	−2.7
		0.5		0.5	0.293	0.295	−0.7
		1.0		1.0	0.567	0.560	+ 1.2
			0.05	0.1	0.066	0.067	−1.5
			0.5	1.0	0.553	0.560	−1.2
	0.5	0.5	0.25	1.0	0.561	0.560	+ 0.2
sulphite-sulphide	—	—	—	0.04	0.030	—	—
	0.05			0.14	0.092	0.093	−1.1
	0.5			1.04	0.575	0.570	+ 0.9
		0.033		0.14	0.096	0.093	+ 3.2
		0.1		0.34	0.209	0.205	+ 2.0
		0.167		0.54	0.319	0.317	+ 0.6
		0.33		1.04	0.570	0.570	0.0
			0.025	0.14	0.095	0.093	+ 2.2
			0.25	1.04	0.580	0.570	+ 1.8
	0.2	0.1	0.075	1.04	0.577	0.570	+ 1.2

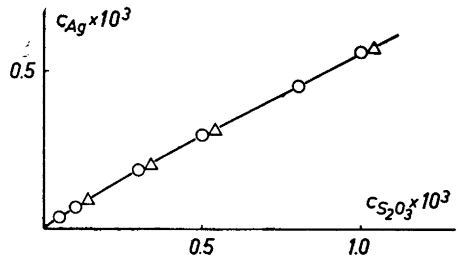

Fig. 1. Standard curve for the determination of thiosulphate by the silver(^{110}Ag) thiocyanate method.
—O— sulphite reaction
—△— sulphite-sulphide reaction.

results in the sulphite series with those in the sulphite-sulphide series, the silver concentrations measured are given in the table instead of the thiosulphate concentrations calculated from the calibration curve. All the concentrations in the table refer to the filtrate obtained after shaking with silver thiocyanate.

The concentrations are given in mole/litre.

Under "calc." are reported the silver contents which were obtained in parallel experiments with thiosulphate.

As may be seen from the table, the agreement between the calibration series with thiosulphate and the actual experiments with polythionates is good. The maximum deviation amounts to 3 %. The results of the sulphite series show, in addition, that the trithionate formed by the reaction does not affect the thiosulphate determination. A comparison of the silver concentrations in the sulphite series and sulphite-sulphide series is not possible in the table since the thiosulphate concentrations in the sulphite-sulphide series are, owing to aerial oxidation of the sulphide, somewhat higher than those in the sulphite series. A comparison between the calibrations with thiosulphate for both of the experimental series has instead been made in Fig. 1. As may be seen from the figure, the agreement between the two series is good which shows that the higher silver content which is obtained in the sulphite-sulphide series can be completely attributed to the amount of thiosulphate which is formed by aerial oxidation of the sulphide.

Influence of hydrogen sulphite at various pH values. In all experiments reported in Table 1, the solution has been acidified with formic acid to pH 4.0 before the determination of thiosulphate. Since the formation of the silver thiosulphate complexes is influenced by the presence of hydrogen sulphite, this effect has been studied as a function of the pH of the solution. The pH interval studied was 2.6—4.9 and the sulphite concentrations were 0.01, 0.05, and 0.1 M. Comparative experiments with thiosulphate solutions in the absence of hydrogen sulphite have also been performed. As is obvious from Table 2, a change in the total sulphite content or in the pH has only a very slight effect on the formation of the silver thiosulphate complexes. The variations in the silver content which have been obtained lie, with exception of the smallest

Table 2. Influence of pH and total sulphite on the determination of thiosulphate.

Temp. °C	c_{SO_3}	$c_{S_2O_3} \times 10^3$ / pH	0.1	0.3	0.5	1.0
			$c_{Ag} \times 10^3$			
24	0.05	2.6	0.070	0.195	0.308	0.575
	0.05	3.5	0.077	0.192	0.320	0.588
	0.10	3.5	0.083	0.198	0.309	0.590
	0.05	4.3	0.068	0.199	0.309	0.573
	0.01	4.3	0.075	0.199	0.310	0.578
	0.05	4.9	0.075	0.199	0.311	0.593
		6.7	0.078	0.214	0.327	0.598
20		2.1	0.075	0.193	0.305	0.550
		4.3	0.075	0.200	0.315	0.580
		6.7	0.078	0.198	0.322	0.575

thiosulphate content, within the experimental error for the method. The acidification after the sulphite reaction can therefore be performed to any pH within the interval 2.6—4.9 without the formation of the silver thiosulphate complexes being thereby appreciably affected. From the comparative experiments performed without the addition of hydrogen sulphite, it is evident that a decrease in the formation of the silver thiosulphate complexes occurs only at a relatively low pH. Whether or not this decrease is due to a decomposition of the thiosulphate added has not been investigated.

Influence of sulphide. For a complete precipitation of sulphide ions as zinc sulphide, it is important to use a freshly prepared zinc carbonate suspension and to filtrate the solution after cooling to room temperature. Otherwise the filtrate will contain a small amount of sulphide ions which give a precipitation of silver sulphide on shaking with solid silver thiocyanate according to

$$2\ AgSCN_{(s)} + S^{2-} \rightarrow Ag_2S_{(s)} + 2\ SCN^-$$

The thiocyanate ions formed in this reaction would then displace the equilibrium between the solid silver thiocyanate and the thiosulphate ions in such a way that the total amount of complex-bound silver would decrease. Some experiments carried out at 24 ± 1°C were performed in order to illustrate how the sulphide and thiocyanate ions affect the formation of the silver thiosulphate complexes. A zinc carbonate suspension was not added in these experiments (*cf.* Table 3). It is seen that the influence of thiocyanate ions is considerable. A corresponding decrease in the total silver content has, however, not been obtained in the presence of sulphide ions. The silver content was found instead to have increased. This is due to the fact that part of the precipitated silver sulphide exists in a colloidal state with such a small particle size that it can pass through even a very fine colloid filter (pore diameter 150 mμ). The presence of silver sulphide in the solution is apparent from its weakly yellow colour.

Table 3. Influence of sulphide and thiocyanate on the determination of thiosulphate.

$c_{S_2O_3} \times 10^3$ / $c_S \times 10^3$	0.3	0.5	1.0
	$c_{Ag} \times 10^3$		
—	0.214	0.327	0.598
—*	0.141	0.220	0.462
0.5	0.322		
0.05	0.287	0.404	

* One μmole KSCN was added per ml solution.

II. THE SULPHIDE(^{35}S) METHOD

In this method, the polythionate solution is first of all allowed to react with an excess of sulphite thus forming thiosulphate as well as one mole of trithionate per mole polythionate (*cf.* eqn. (1) given above). The solution is then made to react at about 100°C with an excess of sulphide containing the radioactive isotope ^{35}S. In this reaction, one mole radioactive thiosulphate is obtained per mole trithionate, *i.e.* one mole radioactive thiosulphate per mole polythionate in the original sample.

The reaction between sulphide and trithionate can be written as follows:

$$S_3O_6^{2-} + {}^*S^{2-} \rightarrow {}^*S_2O_3^{2-} + S_2O_3^{2-}$$

After the remaining sulphide has been precipitated with zinc carbonate, an excess of alkali is added and the thiosulphate and sulphite are oxidized at about 100°C to sulphate by means of hydrogen peroxide. The sulphate is precipitated as barium sulphate and the activity of the precipitate is measured in a proportional counter of the "flow-counter" type. Because the sulphur isotope ^{35}S is a very weak β-emitter ($E_{max} = 0.167$ MeV), the measurements have been performed using the "infinitely thick layer" method. In this method, the thickness of the barium sulphate layer is chosen so that it exceeds the maximum range of the β-radiation. Since the absorption coefficient for β-radiation in barium sulphate is of the order of 0.2 cm^2/mg[8], it can be calculated that the required thickness corresponds to 25 mg $BaSO_4$/cm^2. In this method, the activity measured is proportional to the specific activity of the precipitate. The original amount of polythionate in the sample is, however, proportional to the total activity. A relative measure of the total activity can be obtained by multiplying the measured activity by the total weight of precipitate.

Parallel to the reaction between sulphide and trithionate, radioactive thiosulphate is also formed by isotopic exchange between sulphide and thiosulphate in the following way:

$$*S^{2-} + S{-}SO_3^{2-} \rightarrow *S{-}SO_3^{2-} + S^{2-}$$

This reaction has been studied by Voge [9] who found that the exchange took place very slowly even at 100°C. In the present investigation, it was however found that this exchange is of such a magnitude that it cannot be neglected in the determination of polythionate. Hence, a correction has to be applied if the original sample contains thiosulphate or higher polythionates.

Experimental

Chemicals

Except for the potassium pentathionate, the polythionate preparations have been the same as in the previous section. The pentathionate sample used here contained a relatively large amount of tetrathionate (*cf.* Table 5).

Radioactive sodium sulphide was obtained from the Radiochemical Centre, Amersham, England. The radioactive sulphide solution was prepared by dissolving about 3 mC radioactive sulphide in 1 l 0.25 M inactive sulphide solution containing at most 0.5 mole per cent thiosulphate. In order to determine the relationship between sulphide content and activity, one aliquot of the solution was taken and, after addition of inactive sulphate, oxidized at 90—100°C with hydrogen peroxide. The activity of the precipitated barium sulphate was then measured. Because the sulphide solution contained thiosulphate with a high specific activity, it was necessary to correct the relation between activity and sulphide content for the activity of the thiosulphate. In order to perform this determination, the sulphide was first of all precipitated using zinc carbonate after which the filtrate was treated as above.

Apparatus

In order to obtain reproducible measurements of the activity of the barium sulphate, it is necessary that the precipitate should be spread evenly over a given surface. This has been accomplished by means of a filtration procedure. The suspension of barium sulphate was transferred by means of a slow filtering to a plexiglas crucible provided with a fine filter paper. The inner diameter of the crucible was 3 cm and thus an "infinitely thick layer" could be obtained since the amount of precipitate exceeded 175 mg. When filtering, the plexiglas crucible was mounted between a porcelain muff and a glass sleeve. After filtration and drying, the crucible was placed in a proportional counter in order to measure the activity.

The counter was of the "flow-counter" type. It was equipped with a thin window consisting of a plastic film in order to diminish the comsumption of the gas used for the measurements. This gas was a mixture of 20 % methane and 80 % argon. The counter, amplifier and scaler were manufactured by AB Nukleonikinstrument, Göteborg.

Procedure

To 10—15 ml of the sample, about 5 ml 0.4 M sulphite solution was added after which the liquid was allowed to stand for 15 min at room temperature. Radioactive sulphide solution, 5 ml 0.25 M, was added and the resultant solution was heated in boiling water for 15 min. Then, 10 ml 0.35 M freshly prepared zinc carbonate suspension was added after which the mixture was cooled and filtered. To the filtrate, 5 ml 1 M sodium hydroxide and 10 ml 30 % hydrogen peroxide were added and the solution obtained was heated for 20 min in boiling water. Then, 15 ml 1 M hydrochloric acid was added and, thereafter, an excess of hot 0.2 M barium chloride, dropwise under stirring. After cooling, the solution obtained was filtered in the same way as described above. The precipitate was washed with alcohol and ether and dried at 50°C. The activity and weight of the precipitate were then measured. The activity was corrected for the background radiation. The correction for the radioactive decay was obtained by comparing in each series, the activity

Table 4. Determination of trithionate using the sulphide(^{35}S) method.

Trithionate mmole	Barium sulphate g			Activity, measured c.p.m. × 10^{-3}			Activity × Weight of $BaSO_4$ c.p.m. × g × 10^{-3}			
							Found			Calc.
—	0.458	0.452	0.478	3.30	4.02	4.38	—	—	—	—
0.021	0.473			3.62			0.20			0.20
0.041	0.490			3.85			0.38			0.39
0.103	0.548	0.536	0.565	4.57	5.17	5.40	0.99	0.95	0.96	0.98
0.206	0.632	0.625	0.659	5.48	5.97	6.15	1.95	1.91	1.96	1.96
0.309		0.721	0.752		6.72	6.69		3.03	2.94	2.94
0.412	0.807	0.814	0.847	6.99	7.11	7.18	4.13	3.97	3.99	3.92

obtained with the activity of a standard sample of radioactive barium sulphate. Since it was found to be difficult to transfer the barium sulphate quantitatively to the filter and, at the same time, to obtain a completely even surface, another procedure has also been tried. In it, the barium sulphate suspension was filtered through a glass filter and the weight of the precipitate was obtained. Thereafter, the precipitate was suspended once again in water and then transferred to the plexiglas crucible in order to measure the activity. Hence, in this case, it was not necessary to transfer the precipitate quantitatively to the plexiglas crucible.

Table 5. Influence of thiosulphate upon the determination of polythionates by the sulphide(^{35}S) method.

Polythionate mmole		Thiosulphate mmole	Barium sulphate g	Activity, measured c.p.m. × 10^{-3}	Activity × Weight of $BaSO_4$ c.p.m. × g × 10^{-3}	
		—	0.474	4.44	—	
		0.100	0.516	4.20	0.06	
		0.200	0.563	4.02	0.16	
		0.300	0.610	4.00	0.34	
		0.400	0.656	3.84	0.41	
					Found	*Calc.*
—		—	0.431	3.74	—	—
0.206	$S_3O_6^{2-}$	—	0.633	5.63	1.95	1.96
0.206	$S_3O_6^{2-}$	0.200	0.719	5.20	2.13	2.12
0.206	$S_3O_6^{2-}$	0.400	0.804	4.98	2.39	2.37
—			0.474	4.39	—	—
0.206	$S_3O_6^{2-}$		0.657	6.15	1.96	1.96
0.200	$S_4O_6^{2-}$		0.703	5.80	2.00	2.06
0.2	$S_5O_6^{2-}$ *		0.765	5.87	2.41	2.26
0.041 0.100 0.06	$S_3O_6^{2-}$ + $S_4O_6^{2-}$ + $S_5O_6^{2-}$ *		0.723	5.88	2.17	2.10

* 0.2 mmole of the pentathionate sample contained 0.183 mmole pentathionate and 0.034 mmole tetrathionate.

Results

The radioactive sulphide method has been tried, first of all, for the determination of trithionate. The results are shown in Table 4. The table contains three series which have been performed at intervals of about one month. The values given under "Activity × Weight of $BaSO_4$" have been corrected for the value obtained in the blank measurement. It is seen that a large amount of radioactive thiosulphate is obtained in the blank. This amount of thiosulphate was found already in the original sulphide solution and thus the formation of thiosulphate by aerial oxidation during the heating must be negligible. The more laborious filtration procedure described above (*cf.* under Procedure) has only been used in the third series. It is seen that the difference from the calculated value is least in this series, at most 2 %. In the other two series, it is somewhat larger, *viz.* 5 %.

The mean values obtained for the activity in the three series correspond to a 100 % yield of radioactive thiosulphate which means that the isotope exchange between the radioactive sulphide and the inactive thiosulphate formed by the reaction falls within the experimental error for the method. If, on the other hand, the solution contains thiosulphate at the beginning of the sulphide reaction, the formation of radioactive thiosulphate will be greater. As can be seen from Table 5, this formation of radioactive thiosulphate is proportional to the thiosulphate content and amounts to 10 % of this content. From the experiments with polythionates, it is seen in addition that the isotope exchange between thiosulphate and sulphide occurs independently of the presence of trithionate. This means that, with tetrathionate, a 10 % and, with pentathionate, a 20 % larger amount of radioactive thiosulphate is obtained than in the reaction with trithionate. For a correct determination of the total amount of polythionate, it is therefore necessary to determine, in addition, the total thiosulphate content after the sulphite reaction. This determination can, of course, be performed by means of the ^{110}AgSCN-method but an indirect determination should also be possible by means of the ^{35}S-method. If the latter procedure is used, the solution is oxidized with iodine after the sulphite reaction, and sulphite and radioactive sulphide are thereafter added to the solution as above. The amounts of radioactive thiosulphate formed by means of the original procedure ($*a_2^{I}$) and by means of the modified procedure including oxidation with iodine ($*a_2^{II}$) can be written:

$$*a_2^{I} = \Sigma a_n + 0.1\ [a_2 + \Sigma(n-3)\ a_n]$$
$$*a_2^{II} = \Sigma a_n + 0.55\ [a_2 + \Sigma(n-3)\ a_n]$$

where a_2 and a_n are the amounts of thiosulphate and polythionate $S_nO_6^{2-}$ in the original sample. From these two equations, the amount of polythionate can be calculated as:

$$\Sigma a_n = 1.22\ *a_2^{I} - 0.22\ *a_2^{II}$$

DISCUSSION

In the determination of the total amount of polythionate by the ^{110}AgSCN-method, the uncertainty in the measurement is dependent on the amount of thiosulphate in the original sample and also on $\bar{n}$, the average number of

sulphur atoms per mole polythionate. This is due to the fact that the amount of polythionate is calculated as half the difference between the thiosulphate amounts present in the solution after the sulphite-sulphide and the sulphite reactions. If an excess of thiosulphate is present in the original sample or if $\bar{n}$ is large, the total polythionate content is obtained as a relatively small difference between two large quantities. As appears from the results in Table 1, the largest difference in the determination of thiosulphate amounted to 3 %. From this, it follows that, in a solution which contains only trithionate, the maximum error in the determination of polythionate amounts to 3 %. This error rises to 33 % if the solution also contains, besides trithionate, an amount of thiosulphate which is ten times greater than the amount of the trithionate present. If the solution contains, instead, a higher polythionate, *e.g.* pentathionate, then the maximum error amounts to 9 % if the pentathionate is present alone. In the same way, the error rises to 39 % if the thiosulphate to pentathionate ratio is 10:1.

For a maximum error of 3 % in the thiosulphate determination, the maximum error in $\bar{n}$ can be estimated, according to the conventional calculation of error, to be 10—20 % (for $\bar{n}$ = 3—6) in the case where the sample contains only polythionates. If thiosulphate is present in a ten times larger amount, then the error in $\bar{n}$ is larger.

The determination of polythionates by the ^{35}S-method can be performed with a smaller error than that in the $^{110}AgSCN$-method. The amount of polythionate is obtained in this case as the difference in relative total activity (Weight × Activity of $BaSO_4$; Table 5) between the sample and the blank. Even in the less laborious procedure, the maximum error is less than 5 % despite the relatively high activity in the blank. In the presence of thiosulphate or with higher polythionates, the activity must be corrected for the activity arising from the isotopic exchange between the thiosulphate and sulphide. This correction does not have any appreciable influence on the accuracy of the polythionate determination if the thiosulphate content is determined using the $^{110}AgSCN$-method. The maximum error in the correction will in this case amount to 0.3 % of the thiosulphate content. If the amount of thiosulphate is ten times greater than the amount of trithionate, the maximum error in the polythionates will thus increase from 5 % to 8 %. Due to the greater accuracy in the determination of polythionates by this method, it is clear that the error in $\bar{n}$ will also be smaller. The maximum error in $\bar{n}$ has been calculated to be about 10 %. If, on the other hand, the correction for the isotopic exchange is determined by the ^{35}S-method, the maximum error in the polythionate determination will be much greater. This error increases from 5 % to 19 % if the amount of thiosulphate is ten times greater than the amount of trithionate. The maximum error in $\bar{n}$ also increases in this case.

A further comparison between the two methods shows that, in the ^{35}S-method, the activity is proportional to the amount of polythionate. This is not the case with the $^{110}AgSCN$-method due to the fact that a displacement of the equilibrium between the solid silver thiocyanate and the thiosulphate solution occurs when the concentration is increased. As far as the sensitivity of these methods is concerned, it is seen that the $^{110}AgSCN$-method is sensitive

to much lower contents than the ^{35}S-method. This comparison is of course based on the experimental procedures used as well as on the specific activities of the silver and sulphur which have been employed in this work.

Finally, it should be mentioned that the ^{35}S-method can be used for an indirect determination of thiosulphate. The sample is first oxidized with iodine after which the amount of tetrathionate formed is determined. In the presence of polythionates, it is necessary to perform two determinations, one before and one after the oxidation with iodine. This method has been tested for the determination of thiosulphate in spent liquors from the sulphite cellulose process. The results of these determinations will be published later.

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