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Colorimetric Determination of Thiosulphate in the Presence of Polythionates and Hydrogen Sulphite

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The influence of pentathionate, tetrathionate, trithionate, and hydrogen sulphite upon the colorimetric determination of thiosulphate according to the silver thiocyanate method has been studied. Furthermore, a method for thiosulphate determination based on the reaction between thiosulphate and *p*-benzoquinone, has been worked out. Under proper conditions these additions have only a slight influence.

Colorimetric methods for the determination of thiosulphate have been reported by Utsumi [1,2], Sörbo [3], Straub and Kiss [4], Budd and Bewick [5], and Stolyarov [6].

The first method given by Utsumi (the silver thiocyanate method) is based upon the reaction between solid silver thiocyanate and thiosulphate, which can be written:

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

After separating the solid phase, the amount of thiocyanate can be determined colorimetrically as iron(III)thiocyanate complexes.

In the second method reported by Utsumi (the mercury(II)thiocyanate method) the determination of thiosulphate is based on the formation of thiocyanate in the reaction between thiosulphate and mercury(II) thiocyanate. The reaction may be written:

$$\mathrm{2\ S_2O_3^{2-} + 3\ Hg(SCN)_2 + 2\ H_2O \rightarrow Hg(SCN)_2 \cdot 2\ HgS_{(s)} + 4\ H^+ + 4\ SCN^- + 2\ SO_4^{2-}}$$

Since mercury(II)thiocyanate is very slightly dissociated, it is possible to determine directly the thiocyanate ions formed in this reaction. The determination is made colorimetrically after the addition of iron(III)nitrate.

In the method reported by Sörbo (the cyanide method) thiosulphate reacts with an excess of cyanide at room temperature giving thiocyanate according to the reaction:

$$\mathrm{S_2O_3^{2-} + CN^- \rightarrow SCN^- + SO_3^{2-}}$$

Copper(II)salt is added as a catalyst to the solution. The thiocyanate formed is determined as in the other methods. The cyanide method has also been studied by Straub and Kiss.

In the method given by Budd and Bewick thiosulphate is reduced by tin(II)chloride and aluminium to sulphide. The hydrogen sulphide driven off from the solution is determined colorimetrically by formation of methylene blue with *p*-aminodimethylaniline.

The method given by Stolyarov is based upon oxidizing the thiosulphate by cerium(IV). The amount of thiosulphate is determined indirectly by colorimetrically measuring the decrease of the concentration of cerium(IV). The determination is performed at 365 mμ where cerium(III) does not influence.

The mercury(II)thiocyanate method, the cyanide method, and the method reported by Budd and Bewick, are not applicable in the presence of polythionates since these ions react in a similar way to thiosulphate *. Sulphite also reacts with mercury(II)thiocyanate giving thiocyanate ions. In the presence of sulphite, too high values are also obtained by the silver thiocyanate method [7]. This is due to the formation of complexes containing silver and sulphite ions. Hydrogen sulphite, on the other hand, does not influence this determination, provided that the thiosulphate concentration is higher than 0.5 mM. Sulphite also influences the determination of thiosulphate according to the method by Budd and Bewick, and the method by Stolyarov.

In the present work, the influence of polythionates upon the determination of thiosulphate according to the silver thiocyanate method has been studied. The determination of thiosulphate at extremely low concentrations in the presence of hydrogen sulphite will also be dealt with. A colorimetric method, based on the reaction between thiosulphate and *p*-benzoquinone (the quinone method), is given, and the influence of polythionates and hydrogen sulphite has been studied. The investigation only includes three polythionates: trithionate, tetrathionate, and pentathionate.

I. THE SILVER THIOCYANATE METHOD

Experimental

The shaking- and filtration procedures were performed as described in a previous paper [7]. In the experiments with polythionates and thiosulphate given in Tables 2 and 3, 70 mg solid silver thiocyanate was added to 30 ml of the solution. The thiocyanate dissolved was determined colorimetrically. Ten ml iron(III)nitrate solution, 0.5 M iron(III)-nitrate and 0.5 M nitric acid were added to 15 ml of the filtered test solution. In the other experimental series, 15—20 mg radioactive silver thiocyanate (^{110}Ag being used as a tracer) was added to 30 ml of the solution.

Radioactive silver thiocyanate was used in these experiments in order to make it possible to determine the concentration of silver in the filtrate. The radioactivity measurements were performed in the same way as that described in the previous paper. The colorimetric determination was performed after addition of 5 ml 1.2 M formaldehyde and 5 ml 0.5 M iron(III) nitrate solution to 15 ml of the test solution. This large excess of formaldehyde must be added before the colorimetric determination in order to obtain a stable colour in the solution containing hydrogen sulphite. — A calibration was performed

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* The colorimetric determination of polythionates according to the cyanide method and the mercury (II) thiocyanate method will be described in a forthcoming paper.

with potassium thiocyanate in order to determine the relationship between the absorbance and the concentration of thiocyanate. This calibration gave the absorbance $0.262/10^{-4}$ M thiocyanate. It may be observed that this concentration as well as the concentrations of thiosulphate and polythionates given in Tables 1—3 refer to the solution before the addition of iron(III) nitrate and formaldehyde.

The absorbance was measured at the wave-length 460 mμ by means of a spectrophotometer Beckman Model DU. The slit width was 0.02—0.03 mm and 1 cm cells were used.

In all cases, freshly boiled distilled water was used to obtain stable solutions. Trithionate and tetrathionate were prepared according to Kurtenacker and Matejka[8]. Pentathionate was prepared according to Stamm, Siepold and Goehring[9]. All the salts were more than 97 % pure.

Results

The influence of hydrogen sulphite on the determination of thiosulphate is given in Table 1. The results indicate a decrease in the dissolution of silver thiocyanate which is only to a certain extent compensated for by adding an excess of formaldehyde. In one experiment, the time of shaking was increased from 15 min to 40 min. Despite this increase in the time of reaction, no increase in the dissolution was obtained. This shows that the lower dissolution obtained for solutions containing hydrogen sulphite is not due to a lowered rate of dissolution.

In all experiments given in Table 1, the silver content of the filtrates was also measured in order to make sure that the decreased absorbance really is due to a decreased dissolution of silver thiocyanate. The results show that this explanation holds true although the decrease in dissolution found by the radiometric method is somewhat lower than the effect observed colorimetrically.

In Table 2 the interference of polythionates in the silver thiocyanate method is shown. In these experiments the time of reaction was 10 min and 16 h. For the shorter time of reaction, the dissolution of silver thiocyanate in the polythionate solutions is less than 5 % of the dissolution obtained for thiosulphate. A higher dissolution is obtained, especially for trithionate, upon increasing the time of reaction. After 16 h, the dissolution of silver thiocyanate

Table 1. Influence of hydrogen sulphite upon the determination of thiosulphate according to the silver thiocyanate method.

	Absorbance at the thiosulphate concentration			Silver content, mM at the thiosulphate concentration		
	0.1 mM	0.2 mM	0.3 mM	0.1 mM	0.2 mM	0.3 mM
—	0.207	0.389	0.530	0.078	0.142	0.202
10 mM HSO_3^-	0.174, 0.170*	0.333	0.495	0.070	0.134	0.190
10 mM HSO_3^- + 0.12 M HCHO	0.193	0.352	0.501	0.074	0.138	0.197

* Reaction time: 40 min.

Table 2. Interference of polythionates in the silver thiocyanate method.

Species of ion	Time of reaction	Absorbance at the concentration		
		0.1 mM	0.15 mM	0.20 mM
$S_2O_3^{2-}$	10 min	0.211	0.290	0.392
	16 h	0.518	0.783	—
$S_3O_6^{2-}$	10 min	0.007	0.007	0.008
	16 h	0.079	—	0.098
$S_4O_6^{2-}$	10 min	0.004	0.011	0.012
	16 h	0.018	—	0.020
$S_5O_6^{2-}$	10 min	0.004	0.013	0.016
	16 h	0.022	—	0.034

in 0.1 mM trithionate amounts to 15 % of the value obtained in 0.1 mM thiosulphate. The increased dissolution is probably due to the decomposition of the polythionates and the thiosulphate giving silver sulphide among other things. A short time of reaction must therefore be used for the determination of thiosulphate according to this method.

The dissolution of silver thiocyanate in mixtures of polythionates and thiosulphate has also been studied. The results given in Table 3 show that the increase in the dissolution in the presence of polythionates is less than 5 %.

II. THE QUINONE METHOD

Rzymkowski[10] has investigated a method for the determination of *p*-benzoquinone by titration with thiosulphate in acidic solution. The reaction between *p*-benzoquinone and thiosulphate proceeds, according to Rzymkowski, in three steps.

In the first step the uncoloured hydroquinone monothiosulphuric acid is formed, which in the next step reacts with quinone giving hydroquinone and the yellow quinone monothiosulphuric acid. This reaction was shown to be

Table 3. Influence of polythionates upon the determination of thiosulphate according to the silver thiocyanate method.

Test solution	Absorbance
0.1 mM $S_2O_3^{2-}$	0.211
0.1 mM $S_2O_3^{2-}$ + 0.1 mM $S_3O_6^{2-}$	0.211
0.1 mM $S_2O_3^{2-}$ + 0.1 mM $S_4O_6^{2-}$	0.215
0.1 mM $S_2O_3^{2-}$ + 0.1 mM $S_5O_6^{2-}$	0.220
0.1 mM $S_2O_3^{2-}$ + 0.1 mM $S_3O_6^{2-}$ + +0.1 mM $S_4O_6^{2-}$ + 0.1 mM $S_5O_6^{2-}$	0.215

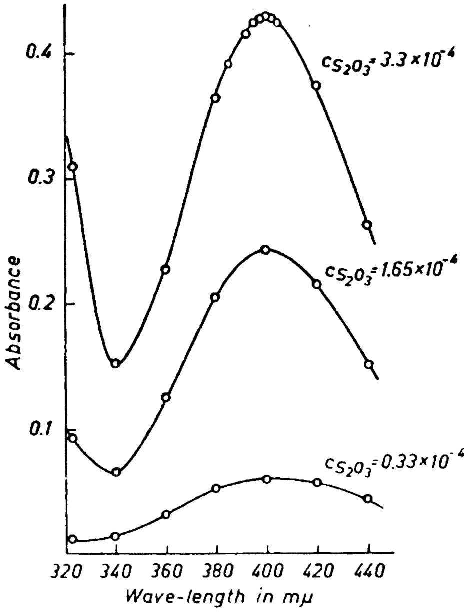

Fig. 1. Absorbance as a function of the wave-length.

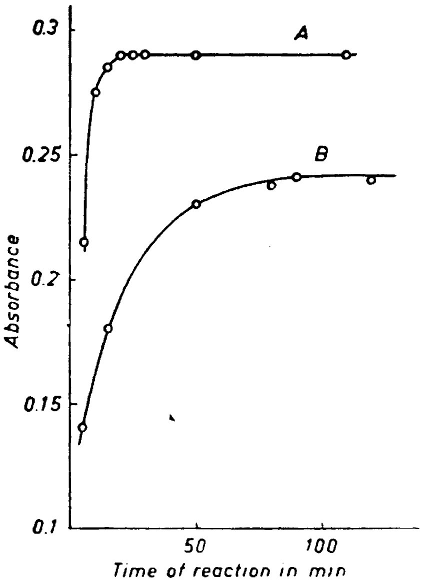

Fig. 2. Absorbance as a function of the time of reaction.

Curve A: 33 mM quinone
Curve B: 3.3 mM quinone

reversible. In the last step, quinone monothiosulphuric acid reacts with thiosulphate giving hydroquinone-2,3-dithiosulphuric acid which is colourless. With excess quinone, this compound is probably further oxidized giving the yellow-red quinone dithiosulphuric acid. With excess quinone the solution is yellow while, with excess thiosulphate, the yellow colour disappears. The reaction has also been studied by Brauer and Staude [11] and Sandved and Holte [12].

The possibility of applying this reaction for the colorimetric determination of thiosulphate at low concentrations has been studied in the present work. The investigation reported here comprises the measurement of absorbance curves and a study of the influence of polythionates, hydrogen sulphite, and formaldehyde on the reaction. The stability of the yellow colour was also studied.

Experimental

For the measurement of the absorbance curves, 10 ml 1.7 M acetic acid and 10 ml 10 mM *p*-benzoquinone were added to 10 ml of 1, 0.5, and 0.1 mM thiosulphate. In the reference solution, the thiosulphate was replaced by 10 ml water. In the other experiments, the addition of acetic acid and *p*-benzoquinone was the same as that above. The slit width was 0.06 mm and 1 cm cells were used in all measurements. The *p*-benzoquinone was of analytical grade, from Dr. T. Schuchardt, München.

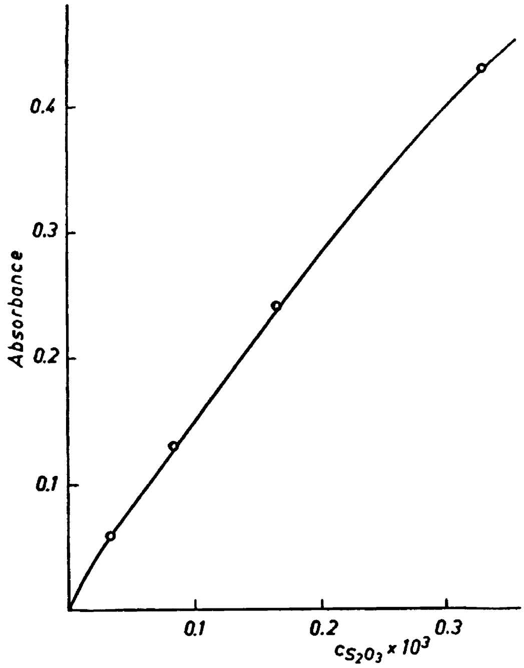

Fig. 3. Absorbance as a function of the concentration of thiosulphate.

Results

In Fig. 1, the absorbance is given as a function of the wave-length in the interval 320—440 mμ. As seen from the figure, the absorbance reaches a maximum at the wave-length 400 mμ.

All the measurements were made 2 h after the addition of the quinone solution since it was found (Fig. 2) that the absorbance increases rapidly until about 90 min after the addition of quinone solution. After this time, the absorbance is constant for at least one hour. The absorbance then decreases by only 6 % during the following 24 h. By increasing the concentration of quinone ten times, *viz.* from 3.3 to 33 mM, a stable absorbance was obtained after only 25 min of reaction. After 24 h, the absorbance was about 7 % less. For this concentrated solution, the absorbance was about 20 % higher than that for 3.3 mM quinone.

From Fig. 3 it is seen that, in the concentration interval 0.33—0.033 mM, the absorbance is not proportional to the thiosulphate content of the solution.

The behaviour of polythionates towards quinone was investigated in the same way as that described for thiosulphate. The absorbance was measured for solutions containing 0.56 M acetic acid, 3.3 mM *p*-benzoquinone, and 0.33 mM polythionate or 0.33 mM polythionate together with 0.165 mM thiosulphate.

Table 4. Influence of polythionates upon the determination of thiosulphate according to the quinone method.

Test solution	Absorbance at 400 mμ
0.33 mM $S_3O_6^{2-}$	0.002
0.33 mM $S_4O_6^{2-}$	0.005
0.33 mM $S_5O_6^{2-}$	0.000
0.165 mM $S_2O_3^{2-}$	0.241
0.165 mM $S_2O_3^{2-}$ + 0.33 mM $S_3O_6^{2-}$	0.242
0.165 mM $S_2O_3^{2-}$ + 0.33 mM $S_4O_6^{2-}$	0.240
0.165 mM $S_2O_3^{2-}$ + 0.33 mM $S_5O_6^{2-}$	0.240

The results in Table 4 show that the polythionates have no effect on the formation of the quinone thiosulphuric acids. As may be seen from Table 5, a considerable influence was obtained when hydrogen sulphite was added. The influence of hydrogen sulphite can, however, be eliminated by the addition of excess formaldehyde. Formaldehyde was in this case also added to the reference solution. At the highest concentration of hydrogen sulphite the absorbance is about 3 % too low despite the addition of formaldehyde. A corresponding decrease in the absorbance is also obtained for solutions containing only formaldehyde and thiosulphate, which shows that the decrease is not due to the presence of hydrogen sulphite. The formation of formaldehyde thiosulphuric acid [13] may to some extent explain the decrease in the absorbance. No experiments have been performed to investigate whether the intermediate compounds formed in the reaction between quinone and thiosulphate react with formaldehyde. The difference in the absorbances obtained for the experiments given in Table 4 and Table 5 may be explained by the fact that different samples of *p*-benzoquinone were used in the two series of experiments.

Table 5. Influence of hydrogen sulphite and formaldehyde upon the determination of thiosulphate according to the quinone method.

$c_{S_2O_3} \times 10^3$	$c_{SO_3} \times 10^3$	$c_{HCHO} \times 10^3$	Absorbance at 400 mμ
0.165	—	—	0.232
0.165	0.165	—	0.202
0.165	0.33	—	0.175
0.165	0.33	4	0.233
0.165	3.3	40	0.233
0.165	33	400	0.225
0.165	—	4	0.232
0.165	—	40	0.230
0.165	—	400	0.222

DISCUSSION

A comparison between the two methods for the determination of thiosulphate shows that the silver thiocyanate method is the more sensitive one, giving about twice the absorbance while, on the other hand, the quinone method is the more specific one since it is not at all influenced by polythionates. In both methods, hydrogen sulphite interferes. This interference is completely eliminated in the quinone method by the addition of formaldehyde while, in the silver thiocyanate method, it can be eliminated only to a certain extent by the addition of formaldehyde. In both methods, the relation between the absorbance and the concentration of thiosulphate is non-linear.

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