

## On the Determination of Thiosulphate by the Silver Thiocyanate Method

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The silver thiocyanate method for the colorimetric determination of thiosulphate has been studied. The relation between the amount of thiosulphate added and the amount of silver thiocyanate dissolved was calculated at the ionic strengths,  $I = 0$  and  $I = 4$ , with the aid of available data on silver thiosulphate complexes. The influence of hydrogen sulphite was also calculated.

Experiments were performed at 20°C for the thiosulphate concentration interval  $2.5 \times 10^{-5}$ — $1.5 \times 10^{-3}$  M and for the sulphite concentrations 0.01 M and 0.1 M. The amount of silver thiocyanate dissolved was determined both colorimetrically and by measuring the radioactivity of the solution,  $^{110}\text{Ag}$  being used as tracer. In the colorimetric method, the absorbance gives the total thiocyanate concentration in the solution since complexes of silver and thiocyanate and mixed complexes of silver, thiosulphate and thiocyanate can be neglected.

The dissolved amount of silver thiocyanate was shown to be constant when shaking for 10—40 min. With longer reaction times, the concentration of thiocyanate increased owing to the formation of silver sulphide.

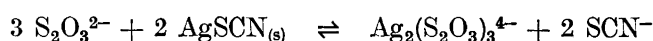
At low ionic strengths, the relationship between thiosulphate added and silver thiocyanate dissolved was linear for  $c_{\text{S}_2\text{O}_3} > 2 \times 10^{-4}$ , while, for lower thiosulphate concentrations, a nonlinear relationship was valid. An addition of 0.1 M hydrogen sulphite did not increase the solubility of the silver thiocyanate.

At  $I = 4$ , the relationship between thiosulphate added and silver thiocyanate dissolved was linear within the whole range of concentration investigated ( $c_{\text{S}_2\text{O}_3} < 5 \times 10^{-4}$ ). It was found that hydrogen sulphite decreased the solubility of silver thiocyanate at this ionic strength. This decrease was almost completely eliminated by the addition of an excess of formaldehyde.

The use of silver azide instead of silver thiocyanate for the determination of thiosulphate in coloured solutions was also studied.

If a solution of thiosulphate is shaken with a solid silver halogenide, the halogenide is dissolved owing to the formation of stable complexes containing silver and thiosulphate ions. This phenomenon is well-known from the

photographic fixing process and many investigations have been published on the dissolution of silver halogenides in complex-forming solutions. On the basis of the photographic fixing reaction, Utsumi<sup>1</sup> has worked out a colorimetric method for the determination of thiosulphate. According to Utsumi, the thiosulphate solution is shaken for some minutes with an excess of solid silver thiocyanate. After separating the solid phase, the amount of thiocyanate dissolved is colorimetrically determined as iron(III)thiocyanate. Utsumi observed that, within the concentration range examined ( $3 \times 10^{-6}$ — $1.8 \times 10^{-4}$  M thiosulphate), the relationship between the thiocyanate and thiosulphate concentrations was linear. Utsumi supposed that the dissolution occurred according to the reaction



In the present paper, this method has been studied more particularly with regard to the determination of thiosulphate in solutions containing hydrogen sulphite. The method is especially designed for analysing thiosulphate in spent liquor from sulphite cellulose cooking. The determination of thiosulphate can be done, in this case, either before or after the separation of high polymer compounds by ion exchange. In the latter case, the low polymer anions are eluted from the anion exchanger with a large amount of 4 M sodium perchlorate. For this reason, the dissolution of silver thiocyanate in thiosulphate has been investigated both for solutions at low ionic strength and for solutions containing 4 M sodium perchlorate.

From investigations published on the thiosulphate in sulphite spent liquor<sup>2</sup>, it can be seen that the thiosulphate concentration amounts to about  $10^{-3}$  M. In the present paper, the silver thiocyanate method has, therefore, been primarily tested for a corresponding concentration range. In solutions containing 4 M sodium perchlorate, a lower concentration range has, however, been of greater interest.

### EXPERIMENTAL

*Chemicals.* Part of the investigation was performed with silver thiocyanate containing <sup>110</sup>Ag. The neutron radiation of a silver wire (puriss) was carried out by AB Atomenergi. The chemicals used were of analytical quality, except for iron(III)nitrate which was puriss grade.

*Shaking- and filtration procedure.* The solution was vigorously shaken (15 min at about 1 500 shakes per min) at  $(20 \pm 0.5)^\circ\text{C}$  with a laboratory "Microid flaskshaker" from Griffin & George Ltd. In the experiments with a longer time of reaction (8–9 h), the solution was rotated (25 r.p.m.) in an air thermostat. When inactive silver thiocyanate was used, 70 mg precipitate was added to 30 ml solution. In the experiments with radioactive silver thiocyanate, the precipitate was dispersed in water or in 4 M sodium perchlorate. A certain volume, 10 or 15 ml, of this mixture was added to the solution. The amount of radioactive precipitate was 15–20 mg per 30 ml solution shaken. The shaking, as well as the other operations, was performed in dark coloured flasks. After shaking, the solutions were immediately filtered through an ultra colloid filter according to Zsigmondy (average pore size 150  $\mu\mu$ ) under a pressure of 2–3 atm nitrogen in a Thiessen apparatus.

*The colorimetric determination.* In the experiments at high ionic strength ( $I = 4$ ), 5 ml iron(III)nitrate solution containing 0.5 M iron(III)nitrate and 0.5 M nitric acid was added to 10 ml of the filtrate. In the experiments at the same ionic strength but in the

presence of hydrogen sulphite, 5 ml 1 M formaldehyde and 5 ml iron(III)nitrate solution were added to 15 ml of the filtrate. The formaldehyde was added in order to bind the hydrogen sulphite. In the experiments at low ionic strengths, the procedure was for  $\text{CS}_2 < 2 \times 10^{-4}$  the same as that described above, while, for a thiosulphate concentration of  $2 \times 10^{-4} - 1.5 \times 10^{-3}$  M, 5 ml iron(III)nitrate solution was added to 10 ml of the filtrate. This latter solution was diluted to 50 ml before the colorimetric determination. In the experiments with hydrogen sulphite, 10 ml 1 M formaldehyde was added before the dilution. The concentration of the iron(III)thiocyanate complexes formed was determined at the wavelength  $460 \text{ m}\mu$  using a spectrophotometer Beckman Model DU. The slit width was  $0.02 - 0.03 \text{ mm}$  and a  $1 \text{ cm}$  cell was used. In each series of experiments, a calibration was performed with potassium thiocyanate in order to determine the relationship between the absorbance and the concentration of thiocyanate. Sodium thiocyanate was used in solutions containing 4 M sodium perchlorate.

*The flame photometric measurements.* In some of the experiments at low ionic strengths, the concentration of sodium was determined by means of a spectrophotometer Beckman Model DU with a flame photometry attachment. The intensity of flame emission was measured at  $589 \text{ m}\mu$ .

*The radioactivity determination.* The activity of 10 ml filtrate was measured with a G.M. tube for liquids, supplied by Mullard Ltd. The radioactivity of the silver thiocyanate was chosen to give about 700 c.p.m./ $10^{-4}$  M silver. Corrections had to be applied for the difference between the radioactive absorptions of solutions of low and high ionic strengths and for the radioactive decay. The scaler was an Electronic Counter PW 4035 from Philips.

*The potentiometric measurements.* The silver electrode was made according to Brown<sup>3</sup>, but with thicker platinum wires in order to obtain larger electrode surfaces. A mercury-(I)sulphate electrode, consisting of a 4 M sodium perchlorate solution saturated with mercury(I)sulphate, served as reference electrode. The potentiometer equipment was obtained from Rubicon Co., Philadelphia and the galvanometer from Leeds & Northrup Co. The measurements were carried out at  $(20 \pm 0.05)^\circ\text{C}$ .

## THEORY

For the quantitative analysis it is of interest to calculate the relation between the total concentrations of thiosulphate and thiocyanate. This calculation has been done on the assumption that solid silver thiocyanate is in equilibrium with the silver thiosulphate complexes in the solution. At the ionic strength  $I = 0$ , the calculation has only been performed for mononuclear complexes since no constants for polynuclear complexes are available in the literature at this ionic strength. The influence of hydrogen sulphite has also been studied. At the ionic strength  $I = 4$ , the calculations can be done more exactly since, in this case, the constants for the polynuclear complexes are known. At this ionic strength, the calculation is divided into two cases. In the first case, the solution is assumed to be supersaturated with  $\text{NaAgS}_2\text{O}_3 \cdot \text{H}_2\text{O}$  whereas, in the second case, this salt is presumed to be in equilibrium with the solution. Whether  $\text{NaAgS}_2\text{O}_3 \cdot \text{H}_2\text{O}$  could precipitate at the lower ionic strength cannot be decided from the literature data<sup>4</sup>.

### Solubility of silver thiocyanate at $I = 0$

Chateau and Pouradier<sup>5</sup> determined potentiometrically the mononuclear dissociation constants at  $20^\circ\text{C}$  for silver thiosulphate complexes. The constants

were recalculated by the authors to the ionic strength  $I = 0$ . From these values, the following complexity constants can be obtained

$$\beta_{1,1} = 6.7 \times 10^8, \beta_{1,2} = 2.9 \times 10^{13} \text{ and } \beta_{1,3} = 1.4 \times 10^{14}.$$

The constants are defined as

$$\beta_{1,n} = \frac{[\text{Ag}(\text{S}_2\text{O}_3)_n^{(2n-1)-}]}{[\text{Ag}^+][\text{S}_2\text{O}_3^{2-}]^n}$$

(All concentrations in the present article are given in mole/litre).

Silver sulphite complexes were studied potentiometrically at 25°C by Chateau, Duranté and Hervier<sup>6</sup>. At the ionic strength  $I = 0$ , the complexity constants can be calculated to be  $\gamma_{1,1} = 4 \times 10^5$ ,  $\gamma_{1,2} = 4.8 \times 10^8$  and  $\gamma_{1,3} = 10^9$ . Chateau *et al.* also showed that the formation of silver sulphite complexes was low in a hydrogen sulphite solution owing to the low concentration of free sulphite. Consequently, all complexes except  $\text{AgSO}_3^-$  can be neglected even in a rather concentrated hydrogen sulphite solution. From the constants for the silver thiosulphate complexes, it is clear that the complex with three ligands is not formed within the actual concentration range  $c_{\text{S}_2\text{O}_3} < 1.5 \times 10^{-3}$ . The concentration of uncomplexed silver ion and the concentrations of silver thiocyanate complexes<sup>7</sup>, mixed silver thiosulphate-thiocyanate complexes (*cf.* under F), the ion pair  $\text{NaS}_2\text{O}_3^-$  and  $\text{HS}_2\text{O}_3^-$  can also be neglected<sup>8</sup>. All these ions can in addition be neglected in the calculations for the ionic strength  $I = 4$ . For the solubility product  $L_{\text{R}} = [\text{Ag}^+][\text{SCN}^-]$ , the value  $1.08 \times 10^{-12}$  has been used<sup>9</sup>.

With these simplifications, the total thiosulphate content is

$$c_{\text{S}_2\text{O}_3} = [\text{S}_2\text{O}_3^{2-}] + [\text{Ag}^+](\beta_{1,1}[\text{S}_2\text{O}_3^{2-}] + 2\beta_{1,2}[\text{S}_2\text{O}_3^{2-}]^2) \quad (1)$$

and the total sulphite content

$$c_{\text{SO}_3} = [\text{SO}_3^{2-}] + \frac{[\text{H}^+][\text{SO}_3^{2-}]}{k_2} + \frac{[\text{H}^+]^2[\text{SO}_3^{2-}]}{k_1 k_2} + [\text{Ag}^+]\gamma_{1,1}[\text{SO}_3^{2-}] \quad (2)$$

where

$$k_1 = \frac{[\text{H}^+][\text{HSO}_3^-]}{[\text{H}_2\text{SO}_3]} \text{ and } k_2 = \frac{[\text{H}^+][\text{SO}_3^{2-}]}{[\text{HSO}_3^-]}$$

The total thiocyanate content is

$$c_{\text{SCN}} = c_{\text{Ag}} = [\text{Ag}^+](\beta_{1,1}[\text{S}_2\text{O}_3^{2-}] + \beta_{1,2}[\text{S}_2\text{O}_3^{2-}]^2 + \gamma_{1,1}[\text{SO}_3^{2-}]) \quad (3)$$

Since  $c_{\text{SCN}} = [\text{SCN}^-]$ , the following relations can be derived from eqns. (1) and (3)

$$c_{\text{S}_2\text{O}_3} = 2[\text{SCN}^-] - \frac{2\gamma_{1,1}L_{\text{R}}}{[\text{SCN}^-]}[\text{SO}_3^{2-}] + \left(1 - \frac{L_{\text{R}}\beta_{1,1}}{[\text{SCN}^-]}\right) \left\{ \left[ \left( \frac{\beta_{1,1}}{2\beta_{1,2}} \right)^2 + \frac{1}{\beta_{1,2}} \left( \frac{[\text{SCN}^-]^2}{L_{\text{R}}} - \gamma_{1,1}[\text{SO}_3^{2-}] \right) \right]^{\frac{1}{2}} - \frac{\beta_{1,1}}{2\beta_{1,2}} \right\} \quad (4)$$

and from (2)

$$[\text{SO}_3^{2-}] = \frac{c_{\text{SO}_3}}{1 + \frac{[\text{H}^+]}{k_2} + \frac{[\text{H}^+]^2}{k_1 k_2} + \gamma_{1,1} \frac{L_{\text{R}}}{[\text{SCN}^-]}} \quad (5)$$

On inserting the values of the constants, eqn. (4) becomes

$$c_{\text{S}_2\text{O}_3} = 2[\text{SCN}^-] - 8.64 \times 10^{-7} \frac{[\text{SO}_3^{2-}]}{[\text{SCN}^-]} + \left(1 - \frac{7.24 \times 10^{-4}}{[\text{SCN}^-]}\right) [(1.33 \times 10^{-10} + 0.0319 [\text{SCN}^-]^2 - 1.38 \times 10^{-8} [\text{SO}_3^{2-}])^{\frac{1}{2}} - 1.16 \times 10^{-5}] \quad (6)$$

The relation  $[\text{SCN}^-] = f(c_{\text{S}_2\text{O}_3})$ , which is of interest here, was calculated numerically from eqn. (6) (cf. Fig. 2). It will be discussed later in connection with the results of the experiments. The solubility function was also calculated for the ionic strengths  $I = 10^{-3}$  and  $I = 10^{-4}$ . It was found that the solubility at these ionic strengths was only a little higher than that at  $I = 0$ . For this calculation, a correction was introduced for the activity factors. The activity factors were calculated according to Debye-Hückel's approximation

$$-\log f_i = \frac{0.5 z_i^2 \sqrt{I}}{1 + \sqrt{I}}$$

The influence of hydrogen sulphite was also estimated from eqn. (6). An addition of 0.1 M hydrogen sulphite, which corresponds to  $[\text{SO}_3^{2-}] \sim 10^{-4}$ , was found not to increase the solubility at the thiosulphate concentration  $10^{-3}$  M while, at  $10^{-4}$  M, the increase in the solubility amounted to 0.7 %. The comparison is made at the same ionic strength. However, if the increase in ionic strength is taken into consideration, then it is found that the solubility will be decreased by the addition of 0.1 M hydrogen sulphite.

#### Solubility of silver thiocyanate at $I = 4$

The dissolution of silver thiocyanate in thiosulphate, with 4 M sodium perchlorate as an additional salt, is somewhat different to that at the ionic strength  $I = 0$ , because of the formation of insoluble  $\text{NaAgS}_2\text{O}_3 \cdot \text{H}_2\text{O}$ . In a solution saturated with  $\text{NaAgS}_2\text{O}_3 \cdot \text{H}_2\text{O}$ , Nilsson<sup>10</sup> found the product  $L_{\text{T}} = [\text{Ag}^+][\text{S}_2\text{O}_3^{2-}] = 5.7 \times 10^{-14}$  at  $I = 4$ . At this ionic strength, the solubility product of silver thiocyanate is  $L_{\text{R}} = 7.76 \times 10^{-13}$  according to Leden and Nilsson<sup>9</sup>. A comparison of these values shows that sodium silver thiosulphate is the more insoluble one. It can, however, be seen from Nilsson's work that  $\text{NaAgS}_2\text{O}_3 \cdot \text{H}_2\text{O}$  precipitates slowly and therefore the calculations must also include the case in which a supersaturated solution is obtained.

#### No formation of $\text{NaAgS}_2\text{O}_3 \cdot \text{H}_2\text{O}$

The complexity constants for silver thiosulphate ions were determined by Nilsson<sup>11</sup> at  $I = 4$  and  $25^\circ\text{C}$ . He found that the measurements could not be explained only by the formation of the mononuclear complexes  $\text{Ag}(\text{S}_2\text{O}_3)_n^{(2n-1)-}$

but also the formation of polynuclear complexes had to be taken into consideration. The best agreement with the experimental results was obtained if the complexes  $\text{Ag}_2(\text{S}_2\text{O}_3)_4^{6-}$  and  $\text{Ag}_{3z}(\text{S}_2\text{O}_3)_{3z+2}^{(3z+4)-}$  were assumed to exist. From the complexity constants  $\beta_{m,n}$  given by Nilsson (*cf.* Ref.<sup>11</sup>, Table 5), it can be calculated that the ions  $\text{Ag}^+$ ,  $\text{Ag}(\text{S}_2\text{O}_3)_3^{5-}$ ,  $\text{Ag}_2(\text{S}_2\text{O}_3)_4^{6-}$  and  $\text{Ag}_3(\text{S}_2\text{O}_3)_5^{7-}$  can be neglected in the concentration range studied here ( $c_{\text{S}_2\text{O}_3} < 5 \times 10^{-4}$ ). The concentration of  $\text{AgS}_2\text{O}_3^-$  is also low but this ion can only be neglected in the upper part of the interval.

If the solution is supersaturated with  $\text{NaAgS}_2\text{O}_3 \cdot \text{H}_2\text{O}$ , then, using the above simplifications, the total silver and thiosulphate contents of the solution can be written:

$$c_{\text{Ag}} = [\text{Ag}^+] \sum_{n=1}^2 \beta_{1,n} [\text{S}_2\text{O}_3^{2-}]^n + \sum_{z=2}^{\infty} 3z\beta_{3z,3z+2} [\text{Ag}^+]^{3z} [\text{S}_2\text{O}_3^{2-}]^{(3z+2)} \quad (7)$$

$$c_{\text{S}_2\text{O}_3} = [\text{S}_2\text{O}_3^{2-}] + [\text{Ag}^+] \sum_{n=1}^2 n\beta_{1,n} [\text{S}_2\text{O}_3^{2-}]^n + \sum_{z=2}^{\infty} (3z+2)\beta_{3z,3z+2} [\text{Ag}^+]^{3z} [\text{S}_2\text{O}_3^{2-}]^{(3z+2)} \quad (8)$$

Since the sum of the polynuclear terms converges very slowly, the whole series must be summed. This summation was performed in Ref.<sup>11</sup> [*cf.* particularly eqns. (48)—(54)] where the constants  $h_0$  and  $h$  were also defined. Upon summation, eqns. (7) and (8) become:

$$c_{\text{Ag}} = \beta_{1,1} [\text{Ag}^+] [\text{S}_2\text{O}_3^{2-}] + \beta_{1,2} [\text{Ag}^+] [\text{S}_2\text{O}_3^{2-}]^2 + \beta_{6,8} [\text{Ag}^+]^6 [\text{S}_2\text{O}_3^{2-}]^8 \times \\ \times \left[ 6 + h_0 \beta_{3,5} [\text{Ag}^+]^3 [\text{S}_2\text{O}_3^{2-}]^3 \frac{(9-6h \beta_{3,5} [\text{Ag}^+]^3 [\text{S}_2\text{O}_3^{2-}]^3)}{(1-h \beta_{3,5} [\text{Ag}^+]^3 [\text{S}_2\text{O}_3^{2-}]^3)^2} \right] \quad (9)$$

$$c_{\text{S}_2\text{O}_3} = [\text{S}_2\text{O}_3^{2-}] + \beta_{1,1} [\text{Ag}^+] [\text{S}_2\text{O}_3^{2-}] + 2\beta_{1,2} [\text{Ag}^+] [\text{S}_2\text{O}_3^{2-}]^2 + \beta_{6,8} [\text{Ag}^+]^6 [\text{S}_2\text{O}_3^{2-}]^8 \times \\ \times \left[ 8 + h_0 \beta_{3,5} [\text{Ag}^+]^3 [\text{S}_2\text{O}_3^{2-}]^3 \frac{(11-8h \beta_{3,5} [\text{Ag}^+]^3 [\text{S}_2\text{O}_3^{2-}]^3)}{(1-h \beta_{3,5} [\text{Ag}^+]^3 [\text{S}_2\text{O}_3^{2-}]^3)^2} \right] \quad (10)$$

Since the complexes are in equilibrium with solid silver thiocyanate, the concentration of free silver ions is  $[\text{Ag}^+] = L_{\text{R}} [\text{SCN}^-]^{-1}$ . For the thiocyanate, it is also valid that  $c_{\text{SCN}} = [\text{SCN}^-] = c_{\text{Ag}}$ . The function  $[\text{SCN}^-] = f(c_{\text{S}_2\text{O}_3})$  can be calculated from these four relations by the trial and error method. The results of this calculation are given in Fig. 4 and are discussed below in connection with the results of the experiments.

#### Formation of $\text{NaAgS}_2\text{O}_3 \cdot \text{H}_2\text{O}$

If  $\text{NaAgS}_2\text{O}_3 \cdot \text{H}_2\text{O}$  precipitates and if this salt is in equilibrium with the solution, then the system will be described by the following two material balances:

$$c_{Ag} = [SCN^-] = [Ag^+] \sum_{n=0}^3 \beta_{1,n} [S_2O_3^{2-}]^n + 2\beta_{2,4} [Ag^+]^2 [S_2O_3^{2-}]^4 + \\ + 3\beta_{3,5} [Ag^+]^3 [S_2O_3^{2-}]^5 + \sum_{z=2}^{\infty} 3z \beta_{3z,3z+2} [Ag^+]^{3z} [S_2O_3^{2-}]^{(3z+2)} + c_s \quad (11)$$

$$c_{s,o_s} = [S_2O_3^{2-}] + [Ag^+] \sum_{n=1}^3 n \beta_{1,n} [S_2O_3^{2-}]^n + 4\beta_{2,4} [Ag^+]^2 [S_2O_3^{2-}]^4 + \\ + 5\beta_{3,5} [Ag^+]^3 [S_2O_3^{2-}]^5 + \sum_{z=2}^{\infty} (3z+2) \beta_{3z,3z+2} [Ag^+]^{3z} [S_2O_3^{2-}]^{(3z+2)} + c_s \quad (12)$$

Since in this case a general function  $c_{s,o_s} = f([SCN^-])$  can easily be derived, the equations will not be simplified as in the calculation for the supersaturated solution. In eqns. (11) and (12),  $c_s$  denotes the amount of  $NaAgS_2O_3 \cdot H_2O$  formed by the reaction. Since the solution is in equilibrium with both solid silver thiocyanate and solid sodium silver thiosulphate, the concentration of free silver is  $[Ag^+] = L_R [SCN^-]^{-1} = L_T [S_2O_3^{2-}]^{-1}$  and the concentration of free thiosulphate is  $[S_2O_3^{2-}] = L_T L_R^{-1} [SCN^-]$ .

After summation and elimination of  $c_s$ ,  $[Ag^+]$  and  $[S_2O_3^{2-}]$ , the following relation is obtained

$$c_{s,o_s} = \left( 1 + \frac{L_T}{L_R} + \beta_{1,2} \frac{L_T^2}{L_R} - \frac{L_R}{[SCN^-]^2} \right) [SCN^-] + 2 \left( \frac{L_T}{L_R} \right)^2 \left[ \beta_{1,3} L_T + \beta_{2,4} L_T^2 + \right. \\ \left. + \beta_{3,5} L_T^3 + \beta_{6,8} L_T^6 \left( 1 + \frac{h_0 \beta_{3,5} L_T^3}{1 - h \beta_{3,5} L_T^3} \right) \right] [SCN^-]^2 \quad (13)$$

and, on inserting the values of the constants:

$$c_{s,o_s} = 0.0429 [SCN^-]^2 + 1.096 [SCN^-] - \frac{7.76 \times 10^{-13}}{[SCN^-]}$$

For the concentration range studied, the first and third term can be neglected and the simple relation  $[SCN^-] = 0.91 c_{s,o_s}$  is obtained.

Whether an addition of hydrogen sulphite will increase the solubility of silver thiocyanate at  $I = 4$  has not been calculated since no complexity constants for this system are available. The influence of this addition was very small at low ionic strengths and is assumed to be of the same order at high ionic strengths.

## RESULTS AND DISCUSSION

*A. Stability of the colour.* On adding the acidic iron(III)solution to the filtrate, there is a risk that the silver thiosulphate complexes will decompose and hence silver thiocyanate will precipitate again. This problem has been studied by measuring the absorbance as a function of time. To 10 ml filtrate ( $c_{s,o_s} \sim 5 \times 10^{-4}$ ), 10 ml iron(III)solution was added. The solution was diluted to 50 ml before the colorimetric determination was performed.

Table 1. Stability of the colour.

| Sample     | Absorbance, after |        |        |        |
|------------|-------------------|--------|--------|--------|
|            | 10 min            | 30 min | 50 min | 90 min |
| $I \sim 0$ | 0.232             | 0.233  | 0.233  | —      |
| $I = 4$    | 0.250             | 0.250  | 0.250  | 0.253  |

The time values in Table I refer to the time passed since the addition of the iron(III)solution. As can be seen from the table, the colour is sufficiently stable to allow a reliable determination of the absorbance. After about 2—3 h, the colour intensity becomes smaller and the solution turns gradually turbid. In solutions containing hydrogen sulphite, a stable colour can only be obtained after the addition of an excess of formaldehyde.

In the following experiments it has been studied whether the measured absorbance really corresponds to the total thiocyanate content in the solution. Two solutions were investigated in this case. One of these consisted of 10 ml silver thiosulphate solution (containing 0.5 mM silver and 1 mM thiosulphate) and 10 ml 0.45 mM potassium thiocyanate, while in the other solution the silver thiosulphate was replaced by 10 ml water. To both solutions 10 ml iron(III)nitrate solution was added. The solutions were diluted to 50 ml and the absorbance was measured. The result of these measurements showed that the absorbance was exactly the same for the two solutions. This means that the colorimetric method gives the total thiocyanate content of the solutions, *i.e.* complexes of silver and thiocyanate and mixed complexes of silver, thiosulphate and thiocyanate can be neglected.

B. *Influence of the shaking time.* The influence of the shaking time has been studied by shaking  $10^{-4}$  M thiosulphate with inactive silver thiocyanate. The results of these experiments (Fig. 1) show that the dissolved amount of thiocyanate remains constant in an interval from 10 to 40 min. Further shaking gives an increased dissolution and, after 8—9 h of rotation, the concentration of thiocyanate reaches a limit  $c_{\text{SCN}} = 2 c_{\text{S}_2\text{O}_3}$ .

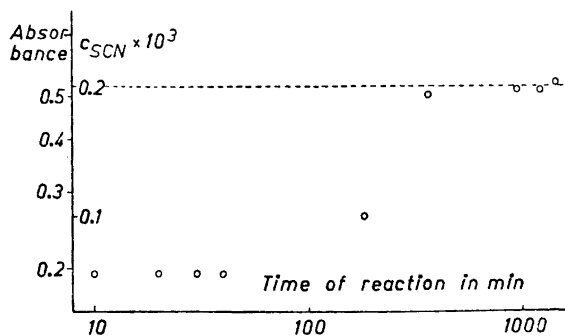


Fig. 1. Dissolution of silver thiocyanate as a function of time of reaction.



The precipitate turns gradually dark during the rotation, indicating a formation of silver sulphide. The dissolution reaction can in this case be written:  $2 \text{AgSCN}_{(s)} + \text{S}_2\text{O}_3^{2-} + \text{H}_2\text{O} \rightarrow \text{Ag}_2\text{S}_{(s)} + \text{SO}_4^{2-} + 2\text{SCN}^- + 2\text{H}^+$ . Whether the experimentally found relation  $c_{\text{SCN}^-} = 2c_{\text{S}_2\text{O}_3}$  is due to a complete transformation of thiosulphate into sulphide and sulphate according to this reaction has not yet been studied. — Similar observations were made by Dickinson<sup>12</sup>, and by Chateau and Pouradier<sup>13</sup> for the dissolution of silver bromide in sodium thiosulphate. — From an analytical point of view, the sample can either be shaken for 10–40 min or rotated for about 8 h. In the latter case, a higher absorbance is obtained and, also, it is probable that the dissolution can be better reproduced. As will be reported in a forthcoming paper<sup>14</sup>, this long time of reaction is not suitable for the determination of thiosulphate in solutions containing polythionates.

C. *Formation of NaAgS<sub>2</sub>O<sub>3</sub> · H<sub>2</sub>O at I ~ 0.* The precipitation of NaAgS<sub>2</sub>O<sub>3</sub> · H<sub>2</sub>O at I ~ 0 was investigated by measuring the sodium content before and after shaking. The determination of sodium was made flame photometrically. The experiments were carried out with  $2 \times 10^{-4}$  M thiosulphate. Parallel determinations of the thiocyanate concentration were performed colorimetrically.

Table 2. Determination of sodium content. Measuring-conditions: O<sub>2</sub>-pressure 15 psi, C<sub>2</sub>H<sub>2</sub>-pressure 4 psi. Slit width 0.01 mm, sensitivity 3.

| Time of shaking<br>min | Sodium concentration |                    | Thiocyanate concentration |                    |
|------------------------|----------------------|--------------------|---------------------------|--------------------|
|                        | Scale divisions      | 10 <sup>-3</sup> M | Absorbance                | 10 <sup>-3</sup> M |
| 0                      | 2.80                 | 0.40               | —                         | —                  |
| 10                     | 2.75                 | 0.39               | 0.377                     | 0.142              |
| 20                     | 2.63                 | 0.38               | 0.377                     | 0.142              |
| 30                     | 2.56                 | 0.37               | 0.380                     | 0.144              |
| 40                     | 2.60                 | 0.37               | 0.377                     | 0.142              |

As is seen from Table 2, the sodium concentration decreases when the reaction time is increased from 10 to 40 min. This decrease cannot be due to an increased formation of NaAgS<sub>2</sub>O<sub>3</sub> · H<sub>2</sub>O since the thiocyanate concentration is constant during this interval of time. The sodium concentration of the filtrate is about 5 % less than that of the original solution. Because this decrease is probably partly caused by an adsorption of sodium ions on the solid silver thiocyanate, the formation of NaAgS<sub>2</sub>O<sub>3</sub> · H<sub>2</sub>O can be considered to be very small. Hence the dissolution of silver thiocyanate at this ionic strength must be due to a formation of complexes with silver ions.

D. *Determination of thiosulphate at low ionic strengths.* The investigations were performed for the thiosulphate concentration interval  $2.5 \times 10^{-5}$ – $1.5 \times 10^{-3}$  M. In Figs. 2 a and 2 b, the results with inactive silver and active silver are compared. The calculated relation  $[\text{SCN}^-] = f(c_{\text{S}_2\text{O}_3})$  is also given in both figures. Fig. 2 a shows the solubility for  $c_{\text{S}_2\text{O}_3} < 1.5 \times 10^{-3}$  while, in Fig. 2 b,

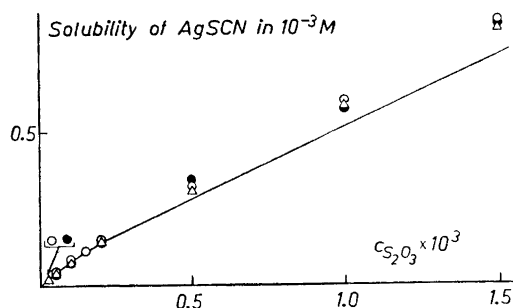


Fig. 2 a. Solubility of silver thiocyanate at low ionic strengths.

- c<sub>SCN</sub>, inactive silver thiocyanate
- c<sub>SCN</sub>, radioactive silver thiocyanate
- △ c<sub>Ag</sub>
- calculated solubility

the solubility for  $c_{S_2O_3} < 2 \times 10^{-4}$  is shown on an enlarged scale. From Fig. 2 a, it is seen that both the calculated and found relationships between the thiocyanate content and the thiosulphate content are linear within a large interval. This linearity does not, however, extend over the whole concentration range investigated.

It can furthermore be seen from the figures that the experiments with inactive and active silver gave the same results despite the fact that these experiments were performed with different amounts of silver thiocyanate. This means that the method is reproducible even if the amount of silver thiocyanate added is varied. This result, as well as the fact that the solubility is independent of the time of shaking, shows that the solid phase is in equilib-

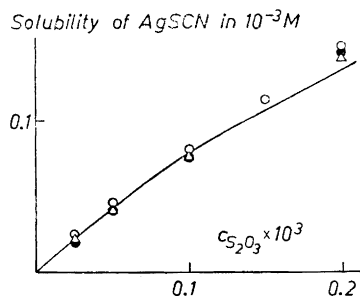


Fig. 2 b. Solubility of silver thiocyanate at low ionic strengths.

- c<sub>SCN</sub>, inactive silver thiocyanate
- c<sub>SCN</sub>, radioactive silver thiocyanate
- △ c<sub>Ag</sub>
- calculated solubility

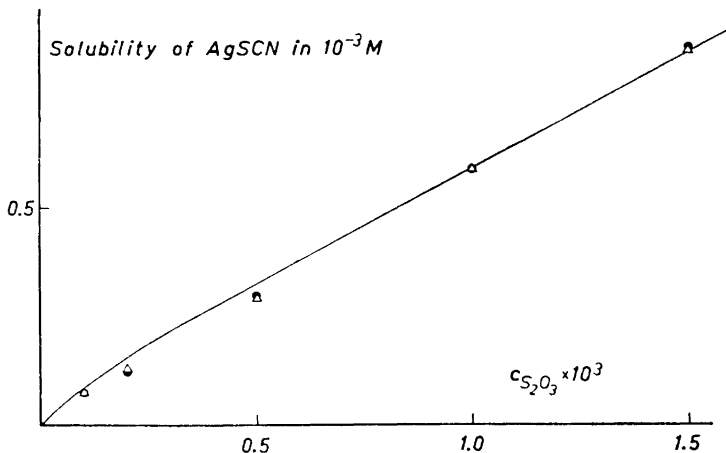


Fig. 3. Solubility of silver thiocyanate in thiosulphate solutions containing 0.1 M hydrogen sulphite.

●  $c_{\text{SCN}}$

▲  $c_{\text{Ag}}$

—solubility determined experimentally in solutions without hydrogen sulphite

rium with the solution. It is also seen that the silver content is equal to the thiocyanate content, which indicates that no solid phase containing silver is formed. The experimentally found curve deviates from the calculated one for  $c_{\text{S}_2\text{O}_3} > 1.5 \times 10^{-4}$  (cf. Fig. 2 b). The calculated values are lower than those found experimentally and the deviation amounts to about 10 %. This deviation is probably due to the formation of polynuclear complexes. These complexes are partly included in the calculated function since the mononuclear dissociation constants<sup>5</sup> were determined without any corrections for polynuclear complexes.

Fig. 3 shows the results of the shaking experiments with thiosulphate and 0.1 M hydrogen sulphite. The curve obtained from the experiments without an addition of hydrogen sulphite is also drawn. It can be seen that the addition of hydrogen sulphite has only a slight influence, as already predicted by the theory. The solubility of silver thiocyanate in a neutral or alkaline sulphite solution is on the other hand considerable. This can be seen from Table 3 which contains the results of the experiments with solutions containing only sulphite.

Table 3. Solubility of silver thiocyanate in sulphite solutions.

| $c_{\text{SO}_3}$ | $c_{\text{Ag}}$      |
|-------------------|----------------------|
| 0.1               | $1.2 \times 10^{-3}$ |
| 0.01              | $4.7 \times 10^{-4}$ |

Summarizing this examination of the silver thiocyanate method at low ionic strengths, it can be said that thiosulphate can be determined in solutions with an excess of hydrogen sulphite but cannot be determined in solutions containing alkaline sulphite. The determination can be performed either colorimetrically or with a method using active silver thiocyanate. For the concentration interval  $c_{S_2O_3} > 2 \times 10^{-4}$  the standard curve  $[\text{SCN}^-] = f(c_{S_2O_3})$  can be approximated by the straight line  $[\text{SCN}^-] = 0.53 c_{S_2O_3} + 0.05 \times 10^{-3}$  which means that the solubility of silver thiocyanate does not increase proportional to the concentration of thiosulphate. For  $c_{S_2O_3} < 2 \times 10^{-4}$  the standard curve deviates considerably from this straight line.

E. *Determination of thiosulphate at high ionic strengths.* A calculation of the function  $[\text{SCN}^-] = f(c_{S_2O_3})$  at ionic strengths up to  $I = 0.1$  indicates that the solubility decreases with increasing ionic strengths. The calculation of this function at higher ionic strengths is, however, difficult with the data available at the present for the complexity constants. In order to investigate the circumstances at various ionic strengths, some experiments with  $10^{-3}$  M thiosulphate were performed. Sodium perchlorate was added to the thiosulphate solution in order to obtain the desired ionic strength (Table 4).

Table 4. Solubility of silver thiocyanate at various ionic strengths.

| $I$   | $c_{Ag} \times 10^3$ | $c_{SCN} \times 10^3$ |
|-------|----------------------|-----------------------|
| 0.001 | 0.58                 | 0.57                  |
| 0.01  | 0.59                 | 0.57                  |
| 0.1   | 0.60                 | 0.58                  |
| 1     | 0.59                 | 0.59                  |

Contrary to the calculated results, the values found experimentally show that the solubility is independent of the ionic strength up to  $I = 1$ .

Particular interest is given in this paper to the course of the dissolution at  $I = 4$ . The investigation at this ionic strength was confined to the concentration range  $c_{S_2O_3} < 5 \times 10^{-4}$ . As in the investigations at the low ionic

Table 5. Solubility of silver thiocyanate at  $I \sim 4$ .

| $c_{S_2O_3} \times 10^3$ | $c_{SO_3} \times 10^3$ | $c_{HCHO} \times 10^3$ | $c_{Ag} \times 10^3$ | $c_{SCN} \times 10^3$ | Absorption coefficient |
|--------------------------|------------------------|------------------------|----------------------|-----------------------|------------------------|
| 0.100                    | —                      | —                      | 0.062                | 0.065                 | 4.58                   |
| 0.200                    | —                      | —                      | 0.114                | 0.127                 | 4.58                   |
| 0.500                    | —                      | —                      | 0.272                | 0.307                 | 4.46                   |
| 0.100                    | 10                     | —                      | 0.036                | 0.048                 | 4.00                   |
| 0.200                    | 10                     | —                      | 0.092                | 0.110                 | 4.00                   |
| 0.500                    | 10                     | —                      | 0.263                | 0.286                 | 4.25                   |
| 0.100                    | 10                     | 200                    | 0.056                | 0.065                 | 4.00                   |
| 0.200                    | 10                     | 200                    | 0.109                | 0.125                 | 4.00                   |

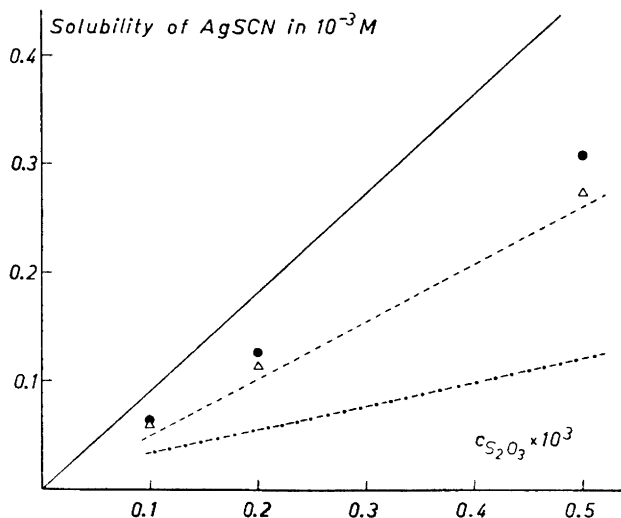


Fig. 4. Solubility of silver thiocyanate at  $I = 4$ .

- $c_{SCN}$
- Δ  $c_{Ag}$
- $c_{SCN}$ , calculated. The solution is assumed to be saturated with  $NaAgS_2O_3 \cdot H_2O$
- calculated solubility. The solution is assumed to be supersaturated with  $NaAgS_2O_3 \cdot H_2O$ .
- ..... calculated concentration of silver bound as mononuclear complexes in the supersaturated solution.

strength the influence of hydrogen sulphite was also studied. The results obtained from these investigations are given in Table 5. The table also contains the absorption coefficients obtained from the experiments with sodium thiocyanate solutions. The unit for the absorption coefficient values is  $10^3 M^{-1} cm^{-1}$ . The results in Table 5 obtained without hydrogen sulphite are plotted in Fig. 4. As is seen from the results, the solubility of silver thiocyanate is considerably decreased by an addition of hydrogen sulphite. This effect can almost be eliminated by adding an excess of formaldehyde. For the analytical application, however, it must be pointed out that, in this case, the relation between the absorbance and the concentration of thiocyanate is not the same as that obtained for solutions without hydrogen sulphite and formaldehyde since a large excess of formaldehyde must be added before the colorimetric determination in order to obtain a stable colour. A corresponding change in the relationship between the absorbance and concentration of thiocyanate is also obtained at low ionic strengths.

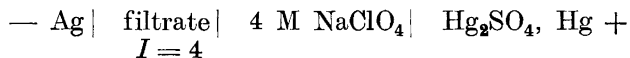
In Fig. 4, the calculated solubility functions  $[SCN^-] = f(c_{S_2O_3})$  are shown. The corresponding relation for the amount of silver, bound as mononuclear complexes in the supersaturated solution, is also presented in the figure. From this relation it can be seen that the amount of silver, bound as polynuclear complexes, is about 50 % of the total silver content. In solutions

saturated with  $\text{NaAgS}_2\text{O}_3 \cdot \text{H}_2\text{O}$ , the silver content is on the other hand very low and follows the equation,  $c_{\text{Ag}} = 0.02 c_{\text{S}_2\text{O}_3} + 1.3 \times 10^{-6}$ , when  $c_{\text{S}_2\text{O}_3} < 5 \times 10^{-4}$ . All the silver is in this case bound as mononuclear complexes. The calculated solubility function, for saturated and supersaturated solutions, can in both cases be approximated by straight lines in the concentration range in question. As already shown in the theory, the relation  $[\text{SCN}^-] = 0.91 c_{\text{S}_2\text{O}_3}$  holds for the saturated solution.

A comparison between the experimentally found values and the calculated ones indicates that the solution is supersaturated with  $\text{NaAgS}_2\text{O}_3 \cdot \text{H}_2\text{O}$ . A small amount of precipitate is, however, formed since the silver content is lower than the thiocyanate content. The agreement between the calculated values and the experimental ones is considered to be acceptable. The calculated values are somewhat lower than the found ones. The experimentally found values also show that the solubility of silver thiocyanate is proportional to the concentration of thiosulphate which can also be seen from the results given in Table 6.

F. *Formation of mixed complexes.* In the investigations reported in literature, the dissolution of silver halogenides in thiosulphate solutions is assumed to occur by the formation of mononuclear silver thiosulphate complexes with various numbers of ligand ions. Yatsimirskii and Panova<sup>15</sup>, however, are of the opinion that the formation of  $\text{AgS}_2\text{O}_3^-$  and  $\text{Ag}(\text{S}_2\text{O}_3)_2^{3-}$  is not so probable. They discuss the problem on the basis of experiments performed by Valenta<sup>16</sup> and consider that the results indicate the formation of the complex  $\text{AgXS}_2\text{O}_3^{2-}$ , where X is the halogenide. Valenta's experiments have also been discussed by Chateau and Pouradier<sup>5</sup>. They determined the mononuclear dissociation constants for  $\text{Ag}(\text{S}_2\text{O}_3)_n^{(2n-1)-}$  and showed, with the aid of these values, that the solubility of the silver halogenides investigated by Valenta is mainly due to the formation of  $\text{Ag}(\text{S}_2\text{O}_3)_2^{3-}$  and  $\text{Ag}(\text{S}_2\text{O}_3)_3^{5-}$ . Whether or not mixed complexes are formed is not discussed by Chateau and Pouradier.

From the results given under A in this work, it is seen that the formation of complexes between silver, thiosulphate and thiocyanate is negligible in solutions containing a large excess of iron(III)ion. The question whether mixed complexes exist in the filtrates from the shaking experiments (before the addition of iron(III)nitrate) has been studied in the present work by measuring the concentration of free silver ion  $[\text{Ag}^+]$  and the total content of thiocyanate. The experiments were performed at the ionic strength  $I = 4$  using inactive silver thiocyanate. For the potentiometric determination of the concentration of free silver ion, the cell can be written:



The emf (in mV) of this cell is at 20°C

$$E = E_0 - 58.17 \log [\text{Ag}^+] = -81.3 - 58.17 \log [\text{Ag}^+]$$

The value of  $E_0$  was determined in a cell where the filtrate was replaced by silver perchlorate solutions of known concentrations. Sodium perchlorate was added to these solutions to make ionic strength  $I = 4$ . This determination

also gave a check that the electrodes followed Nernst's law. No corrections for the diffusion potentials were made since the ionic mobilities of the complexes formed were not known. The results are given in Table 6. Two series are reported — in the first, the experiments were performed with an aged precipitate while, in the latter, the precipitate was freshly prepared.

Table 6. Determination of  $[Ag^+]$ .

| $cs_2O_3 \times 10^4$ | $c_{SCN} \times 10^4$ | $E$   | $[Ag^+] \times 10^9$ | $[Ag^+] c_{SCN} \times 10^{13}$ | $c_{SCN} / cs_2O_3$ |
|-----------------------|-----------------------|-------|----------------------|---------------------------------|---------------------|
| 1.00                  | 0.59                  | 375.5 | 14.0                 | 8.3                             | 0.59                |
| 2.00                  | 1.17                  | 397.1 | 5.97                 | 7.0                             | 0.59                |
| 5.00                  | 2.97                  | 423.8 | 2.08                 | 6.2                             | 0.59                |
| 1.00                  | 0.61                  | 376.9 | 13.3                 | 8.1                             | 0.61                |
| 2.00                  | 1.17                  | 398.1 | 5.74                 | 6.7                             | 0.59                |
| 3.50                  | 2.11                  | 414.9 | 2.95                 | 6.2                             | 0.60                |

If mixed complexes exist in the filtrate the product  $c_{SCN} [Ag^+]$  will be higher than the solubility product of silver thiocyanate. The product  $c_{SCN} [Ag^+]$  will in addition increase with the concentration of thiosulphate and thiocyanate, since the formation of the mixed complexes also increase. From Table 6 it is seen that the calculated product decreases with increasing thiosulphate concentration. In comparison with the value for the solubility product  $L_R = 7.76 \times 10^{-13}$  given by Leden and Nilsson, all the calculated values are too low except those for the lowest concentration of thiosulphate. Consequently it cannot be shown by these experiments whether or not mixed complexes are formed. On the other hand, the potentiometric measurements and the experiments performed with radioactive silver indicate that the concentration of mixed complexes in the filtrate is considerably lower than predicted by Yatsimirskii and Panova.

From Table 6 it is seen that the dissolution is independent of the age of the precipitate. The calculated ratio  $c_{SCN}/c_{S_2O_3}$  shows the linearity of the dissolution function.

G. *Determination of thiosulphate using other insoluble salts than silver thiocyanate.* The determination of thiosulphate as reported above is not limited to the use of silver thiocyanate. Utsumi<sup>17</sup> has also used copper(I)thiocyanate for the determination. In this case, Utsumi suggests an addition of 0.3 ml 6 N nitric acid to 10 ml of the sample before the shaking procedure in order to obtain a higher solubility. In the present investigation it was shown that, with such an addition, the solubility was very high even without the addition of thiosulphate. In a neutral thiosulphate solution, the solubility of the copper(I)thiocyanate was found to be lower than the solubility of silver thiocyanate at a corresponding thiosulphate concentration.

By using radioactive silver salts, the analytical method is not limited to those compounds where the solubility can be determined colorimetrically. Silver chloride, bromide and iodide can be employed. The solubility of silver

iodide is, however, too low from an analytical point of view. For dark coloured solutions, the method with radioactive silver is of course the only suitable one. In certain cases, a colorimetric method is available for dark coloured solutions if silver azide is used as solid salt. In this case, the filtrate is steam distilled in a Parnas<sup>18</sup> apparatus after addition of sulphuric acid. The volatile hydrazoic acid is driven off by the distillation and is subsequently absorbed in a receiver containing acidic iron(III)nitrate solution. Like thiocyanate, the azide ion forms coloured complexes with the iron(III)ion. These complexes have an absorption maximum at the wave-length 460  $\mu$ . Since the hydrazoic acid is a weak acid ( $K_a = 2.6 \times 10^{-5}$ ) and since the silver azide is comparatively soluble ( $L = 2.6 \times 10^{-9}$ ), the use of silver azide is limited to weakly alkaline solutions which do not contain sulphite. The distillation procedure was tested in the present work. It was found that hydrazoic acid was completely driven off by passing 50 g steam through 30 ml 1 mM azide solution to which 2 ml 5 N sulphuric acid had been added. The relationship between added thiosulphate and dissolved silver azide was found to be nonlinear.

The author wishes to thank Docent I. Leden and Dr. R. O. Nilsson for valuable discussions and Mr. E. Seyfarth for assistance with the laboratory work. *Statens Tekniska Forskningsråd* and *Chalmerska Forskningsfonden* have supported the research financially, which support is gratefully acknowledged.

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Received June 9, 1958.