

## Indirect Determination of Thiosulphate in Water by Atomic Absorption Spectrometry

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A simple procedure for indirect atomic absorption spectrometric (AAS) determination of trace thiosulphate has been described. Thiosulphate ions form complex with silver ions. Silver thiosulphate complex is completely floated by oleic acid (HOL) surfactant at  $\text{pH} \leq 3$  in nitric acid medium. The procedure depends on adding known excess of  $\text{Ag}^+$  to the analyte  $\text{S}_2\text{O}_3^{2-}$  solution. After flotation, under the optimum conditions, the unfloted  $\text{Ag}^+$  is directly determined by AAS. The effects of some cations, anions and temperature on the flotation efficiency of silver thiosulphate and determination of excess silver have been examined. The procedure was successfully extended to determine trace thiosulphate added to tap water.

### INTRODUCTION

In the literature, there are several procedures dealing with indirect determination of anions<sup>1-3</sup>. Westerland-Helmerson<sup>4</sup> determined chloride content in lead and zinc oxides indirectly by precipitation as silver chloride. The precipitate was dissolved in ammonia and then determined directly for silver and indirectly for chloride by atomic absorption spectrometry (AAS.) Recently, Granzhan and Charykov<sup>5</sup> extracted silver thiosulphate and determined silver in organic phase by AAS. However, these procedures are time consuming and may have problems arising from background absorbance of the extractable organic solvent in the flame. According to the foregoing discussion, our attention is focused towards combining flotation technique with AAS for anion determination owing to the simplicity and time saving.

The present work reports a novel approach for indirect determination of thiosulphate by adding excess silver, floating as silver thiosulphate and determining the unfloted silver directly by AAS.

### EXPERIMENTAL

All glassware was soaked overnight in 50% sulphuric acid, rinsed thoroughly before use with double distilled water and dried in a dust-free atmosphere. The

flotation cell was a test tube of 12 mm inner diameter and 290 mm long with a stopcock at the bottom. Perkin-Elmer Atomic Absorption Spectrometer 2380 was used for silver determination. The pH measurements were carried out with HANNA Instruments 8519 digital pH-meter.

All chemicals used were of AnalaR and BDH grades. The aqueous solutions were prepared in double distilled water.

*Silver stock solution* ( $0.1 \text{ mol l}^{-1}$ ): 1.6987 g of silver nitrate was dissolved in 100 ml double distilled water.

*Thiosulphate stock solution* ( $0.1 \text{ mol l}^{-1}$ ): 2.4809 g of sodium thiosulphate ( $\text{Na}_2\text{S}_2\text{O}_3 \cdot 5\text{H}_2\text{O}$ ) were dissolved in one litre of water.

*Oleic acid (HOL) stock solution* ( $6.36 \times 10^{-2} \text{ mol l}^{-1}$ ): 20 ml of HOL, food grade, (d 0.895) were dispersed in one litre of kerosene.

## Procedure

Into the flotation cell, 20 mL of a solution containing a defined amount of  $\text{S}_2\text{O}_3^{2-}$ ,  $\text{HNO}_3$  for controlling pH, known excess of  $\text{Ag}^+$  and HOL were introduced. The flotation cell containing the solution was slowly and repeatedly turned upside down about twenty times by hand. Few seconds are required for complete flotation of silver thiosulphate complex. The excess silver in the underlying liquid was determined by atomic absorption spectrometry at 328.1 nm wavelength. Knowing the concentration of unfloated silver (excess) and floated (equivalent to thiosulphate) the concentration of thiosulphate can be calculated in the original solution.

The influence of temperature on the flotation efficiency of silver thiosulphate complex was examined.  $\text{S}_2\text{O}_3^{2-}$ ,  $\text{Ag}^+$  and HOL solutions were either heated or cooled to the required temperature. The silver and HOL solutions were quickly poured into the thiosulphate solution at time zero. The solution was introduced into the flotation cell jacketed with 1 cm thick fibre glass insulation. The procedure of flotation mentioned before was followed. Because the flotation was complete in few seconds, the insulation of the cell (no thermostating) has no effect on the flotation process as has been described<sup>6</sup>

The measurements were carried out at room temperature, about 25°C.

## RESULTS AND DISCUSSION

### Effect of pH

Figure 1 shows floatability of silver ions,  $1.0 \times 10^{-5} \text{ mol l}^{-1}$  with HOL,  $6.36 \times 10^{-4} \text{ mol l}^{-1}$ , at different pH values. It can be seen that the flotation efficiency of  $\text{Ag}^+$  ions is zero at  $\text{pH} < 3$ . The flotation efficiency increases gradually at  $\text{pH} > 3$  reaching its maximum at pH 4 and again decreases.

Figure 2 shows the floatability of silver thiosulphate complex with HOL,  $6.36 \times 10^{-4} \text{ mol l}^{-1}$ , as a function of pH using  $\text{Ag}^+$ ,  $1.0 \times 10^{-5} \text{ mol l}^{-1}$  and  $\text{S}_2\text{O}_3^{2-}$ ,  $0.5 \times 10^{-5} \text{ mol l}^{-1}$ . As may be seen, a maximum flotation efficiency (100%) of  $\text{Ag}_2\text{S}_2\text{O}_3$  is obtained at  $\text{pH} \leq 3$ . The floatability of  $\text{Ag}_2\text{S}_2\text{O}_3$  again decreases at  $\text{pH} > 3$ .

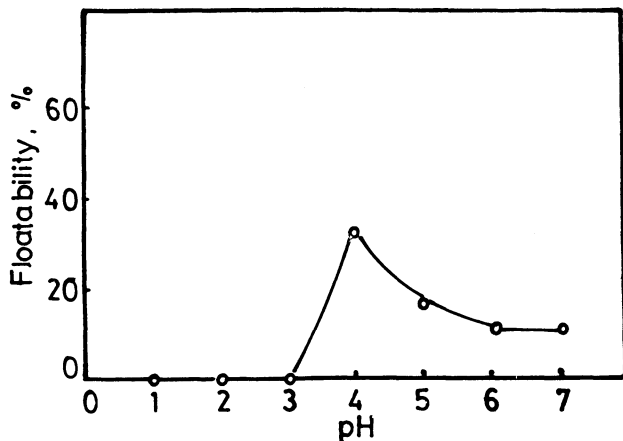


Fig. 1 Floatability of  $\text{Ag}^+$  vs pH,  $\text{Ag}^+$ ,  $1.0 \times 10^{-5} \text{ mol l}^{-1}$  and HOL,  $6.36 \times 10^{-4} \text{ mol l}^{-1}$

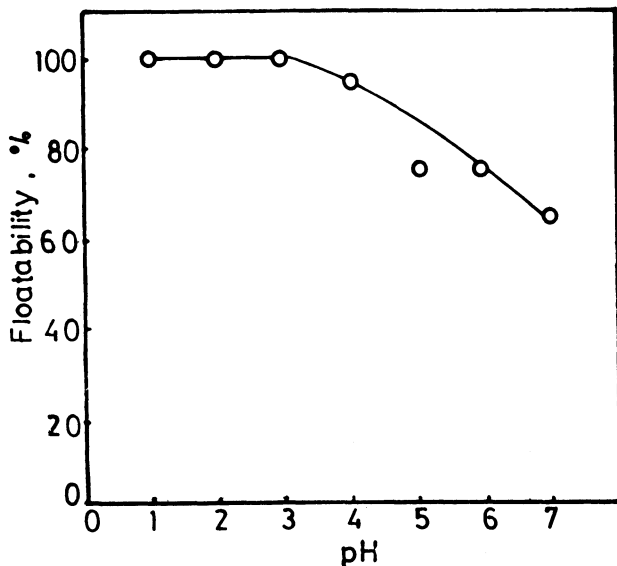


Fig. 2 Floatability of  $\text{Ag}_2\text{S}_2\text{O}_3$  vs pH,  $\text{Ag}^+$ ,  $1.0 \times 10^{-5} \text{ mol l}^{-1}$ ;  $\text{S}_2\text{O}_3^{2-}$ ,  $0.5 \times 10^{-5} \text{ mol l}^{-1}$  and HOL,  $6.36 \times 10^{-1} \text{ mol l}^{-1}$

Comparing figures 1 and 2 we may conclude that silver ions are completely floated as  $\text{As}_2\text{S}_2\text{O}_3$  (white precipitate), in which the ratio of  $\text{Ag}^+$  to  $\text{S}_2\text{O}_3^{2-}$  is 2 : 1, at  $\text{pH} \leq 3$ . Moreover, the colour of silver thiosulphate changes gradually in the scum from white to black  $\text{Ag}_2\text{S}$ . This may be due to hydrolysis according to the following equation:



in which the ratio of  $\text{Ag}^+$  to  $\text{S}^{2-}$  is still 2 : 1. This may also confirm that the interaction between oleic acid surfactant and the precipitate is of an electrostatic

(not chemical) type since the silver thiosulphate and silver sulphide are characterized by their colloidal properties. From the above discussion, the pH of measurements was fixed with  $\text{HNO}_3$  at  $\text{pH} < 3$ .

### Effect of Some Foreign Ions

An extensive series of experiments were carried out to study the effect of some cations (*ca.* Na, K, Mg, Ca, Ba, Pb, Zn, Al, Bi, Mn, Co and Ni) and some anions (*ca.*  $\text{SO}_4^{2-}$ ,  $\text{PO}_4^{3-}$ ,  $\text{NO}_2^-$ ,  $\text{Cl}^-$ ,  $\text{Br}^-$  and  $\text{I}^-$ ) on flotation efficiency of  $\text{Ag}_2\text{S}_2\text{O}_3$  and determination of unfloatable  $\text{Ag}^+$  by AAS. It was found that the studied cations or anions have no effect on floatability of  $\text{Ag}_2\text{S}_2\text{O}_3$ . Moreover, if the studied halides precipitate the corresponding silver halide it will dissolve again in thiosulphate solution<sup>7,8</sup>. Also, since these silver halide precipitates are colloidal they are floated with HOL.

The anions carbonate, nitrite and phosphate have no effect on silver determination by AAS, since their precipitates with silver are soluble in  $\text{HNO}_3$  used for controlling pH. Sulphate anion does not interfere with silver determination by AAS except at high concentration and temperature since it forms insoluble<sup>8</sup>  $\text{Ag}_2\text{SO}_4$ . The  $\text{Cl}^-$ ,  $\text{Br}^-$  and  $\text{I}^-$  anions do not interfere with silver determination by AAS to a limited concentration ( $< 10^{-3} \text{ mol l}^{-1}$ ). Above this concentration, these halides interfere with silver determination by AAS.

### Effect of temperature

A series of experiments were conducted to study the effect of temperature on the flotation efficiency of silver thiosulphate. The separation-flotation of  $\text{Ag}_2\text{S}_2\text{O}_3$  was successful (100%) at temperature ranges from  $10^\circ$ – $80^\circ\text{C}$  using  $\text{Ag}^+$ ,  $1 \times 10^{-5} \text{ mol l}^{-1}$ ;  $\text{S}_2\text{O}_3^{2-}$ ,  $0.5 \times 10^{-5} \text{ mol l}^{-1}$  and HOL,  $6.36 \times 10^{-4} \text{ mol l}^{-1}$  at pH 1. It seems that raising temperature develops the flotation process which may be due to coagulation precipitation.

### Application to tap water

In order to investigate the applicability of this method to tap water, the flotation of known amounts of  $\text{S}_2\text{O}_3^{2-}$ , as  $\text{Ag}_2\text{S}_2\text{O}_3$ , added to tap water taken up from five

TABLE I  
DETERMINATION OF THIOSULPHATE IN TAP WATER SAMPLES USING  $\text{Ag}^+$ ,  
 $1.0 \times 10^{-5} \text{ mol l}^{-1}$  AS A PRECIPITANT AND HOL,  $6.36 \times 10^{-4} \text{ mol l}^{-1}$   
AS A SURFACTANT AT pH 1\*

Sample Number	$\text{S}_2\text{O}_3^{2-} \text{ mol l}^{-1}$		Absolute error	Relative error
	added	found		
1	$0.50 \times 10^{-5}$	$0.50 \times 10^{-5}$	zero	zero
2	$0.50 \times 10^{-5}$	$0.48 \times 10^{-5}$	$0.02 \times 10^{-5}$	4
3	$0.50 \times 10^{-5}$	$0.51 \times 10^{-5}$	$0.01 \times 10^{-5}$	2
4	$0.50 \times 10^{-5}$	$0.50 \times 10^{-5}$	zero	zero
5	$0.50 \times 10^{-5}$	$0.49 \times 10^{-5}$	$0.01 \times 10^{-5}$	2

\* $\text{HNO}_3$  was used for controlling pH.

different locations were examined by the above procedure. 20 mL aliquots of tap water containing  $0.5 \times 10^{-5} \text{ mol l}^{-1} \text{ S}_2\text{O}_3^{2-}$ ,  $1.0 \times 10^{-5} \text{ mol l}^{-1} \text{ Ag}^+$  and  $6.36 \times 10^{-4} \text{ mol l}^{-1} \text{ HOL}$  were floated at pH 1. The pH of the solution was adjusted with  $\text{HNO}_3$ . Table 1 lists the data obtained. The data indicate that the process has a satisfactory determination of  $\text{S}_2\text{O}_3^{2-}$  at pH 1 using  $\text{Ag}^+$  as a precipitant and HOL as a surfactant.

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