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## Note

### Thiomercurimetric determination of thiosulphate and polysulphanedisulphonates on pherograms

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There are established methods for the satisfactory separation of polysulphane-disulphonates (polythionates)<sup>1</sup>, but the methods suggested for the quantitative determination of the separated compounds seem to be of limited practical interest. A coulometric method following conversion into thiosulphate<sup>2</sup>, a densitometric method following conversion into silver sulphide<sup>3</sup> and a radiometric procedure based on the measurement of the activity of <sup>35</sup>S-labelled polysulphanedisulphonates<sup>4</sup> have been described.

The method presented here depends on the reaction of thiosulphate and polysulphanedisulphonates with mercury(II) chloride:



and



The excess of mercury(II) chloride is removed in a stream of water and the mercury content of the spots is determined using titration with soluble zinc sulphide in the presence of dithiofluorescein as indicator. In this way, the relative concentrations of the separated substances can be found and, assuming that the analysis of the original solution for thiosulphate and total polysulphanedisulphonates content has been carried out, the true concentration of every constituent can be calculated.

## EXPERIMENTAL

Polysulphanedisulphonates were prepared according to published methods<sup>5</sup> and aqueous solutions were analyzed by the method of Jay<sup>6</sup>. The separation by ionophoresis was carried out on Whatman No. 1 paper placed between two water-cooled plastic-covered plates, at 60 V/cm and 2 mA/cm for 80 min. The electrolyte consisted of 0.05 M trisodium citrate in 20% ethylene glycol, pH 6.0.

The relative mobilities with regard to thiosulphate were  $\text{S}_3\text{O}_6^{2-}$  0.92,  $\text{S}_4\text{O}_6^{2-}$  0.81,  $\text{S}_5\text{O}_6^{2-}$  0.74 and  $\text{S}_6\text{O}_6^{2-}$  0.65.

The quantitative determination was carried out as follows. The partially dried pherogram was moistened with saturated mercury(II) chloride solution and dried at 70°. The paper was then placed in a flat vessel, treated with dilute acetic acid, washed

with a stream of water for 20 min, treated with saturated sodium chloride solution, washed for 10 min, treated again with saturated sodium chloride solution, washed for 10 min, treated with 0.1 *M* potassium iodide solution, washed for 10 min, and finally treated with 0.1 *M* potassium iodide solution and washed for 10 min. The paper was then dried, treated with 0.05 *M* sodium sulphide solution, neutralized with acetic acid to the phenolphthalein end-point and washed with water. The black spots on the paper were cut out, attached separately to small glass hooks and placed for 2 min in a vessel containing bromine vapour (the papers must be moist), then dried at 35°, placed in a test-tube, moistened with two drops of *ca.* 0.05 *M* sodium sulphite solution, treated with 2 ml of a solution containing 10 g/l of EDTA-Na<sub>2</sub> in 0.5 *M* potassium hydroxide solution and titrated slowly in the presence of 0.2 ml of indicator solution against 10<sup>-4</sup>–5·10<sup>-4</sup> *M* soluble zinc sulphide to the blue end-point. When dealing with very small concentrations, the mercury content of the background (*ca.* 5·10<sup>-3</sup> μmole/cm<sup>2</sup>) should be determined, the area of the cut-out spots measured and a correction calculated.

The zinc sulphide solution was prepared as follows. A 3-g amount of soluble starch was dissolved in 200 ml of boiling water, the mixture was cooled 150 ml of 0.05 *M* zinc sulphate solution and 100 ml of 2.5 *M* sodium hydroxide solution were added and the solution was diluted to 500 ml. To a well-agitated 50-ml portion of this solution were added slowly 5–25 ml of 0.01 *M* sodium sulphide in 0.1 *M* sodium hydroxide solution and the mixture was diluted to 500 ml with water. The clear solution obtained is stable and resistant to air oxidation. The exact concentration can be determined either by titration with *o*-hydroxymercuribenzoic acid<sup>7</sup> or by titration of a standard solution of a mercury salt.

The indicator solution was prepared as follows. To 1 ml of *ca.* 0.005 *M* mercury(II) chloride or nitrate were added 1 ml of 0.1 *M* EDTA-Na<sub>2</sub> solution and 2 ml of 0.1 *M* sodium hydroxide solution and a solution containing 5 mg of dithiofluorescein in 25 ml of 0.02 *M* sodium hydroxide was added until a blue colour was obtained. The mixture was then diluted to 50 ml and kept in the dark.

## RESULTS

Eight solutions of concentration ranging from 0.005 to 0.05 *M* were prepared for every compound, and 0.02 ml of each solution were placed on the paper without loss. The paper was treated as described above. The solution of electrolyte did not interfere in the determination. The results are given in Table I.

TABLE I

MOLE RATIO OF THE MERCURY CONTENT IN THE SPOT TO THE SULPHUR COMPOUND PLACED ON THE PAPER (0.2–1.0 μmole)

<i>Sulphur compound</i>	<i>Mean value,</i> <i>n = 8</i>	<i>Standard deviation,</i> <i>n = 8 (%)</i>
Na <sub>2</sub> S <sub>2</sub> O <sub>3</sub>	1.48	3.7
K <sub>2</sub> S <sub>3</sub> O <sub>6</sub>	1.46	4.6
K <sub>2</sub> S <sub>4</sub> O <sub>6</sub>	1.50	3.5
K <sub>2</sub> S <sub>5</sub> O <sub>6</sub>	1.47	3.8
K <sub>2</sub> S <sub>6</sub> O <sub>6</sub>	1.44	4.0

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