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# Iodimetric Determination of Tetrathionate and Simultaneous Determination of Thiosulfate and Tetrathionate

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The method of iodimetric determination of tetrathionate and simultaneous determination of thiosulfate and tetrathionate in one sample is described. Tetrathionate in alkaline medium ($c(NaOH) = 5$ mol $l^{-1}$) is stoichiometrically converted into thiosulfate and sulfite, which react with iodine. In the volumetric titration with the potentiometric end-point detection the determination range is 10–800 μmol for tetrathionate. In the first stage simultaneous determination of thiosulfate and tetrathionate, thiosufhate is oxidized in neutral medium with iodine to tetrathionate. In the second stage the total content of tetrathionate in alkaline medium is iodimetrically determined. The proposed method allows the determination of both compounds in the range from 30 to 400 μmol in a sample with relative accuracy ±1%.

Opracowano metodę jodymetrycznego oznaczania czterotionianu oraz współoznaczania tiosiarczanu i czterotionianu w jednej próbce. Czterotionian w środowisku zasadowym ($c(NaOH) = 5$ mol $l^{-1}$) jest stechiometrycznie przekształcany w tiosiarczan i siarczyn, które reagują z jodem. W miareczkowaniu objętościowym z potencjometryczną detekcją punktu końcowego oznaczono 10–800 μmoli czterotionianu. Przy współoznaczaniu tiosiarczanu i czterotionianu w pierwszym etapie wykorzystano reakcję utleniania tiosiarczanu do czterotionianu jodem w środowisku obojętnym. W drugim etapie oznaczano jodometrycznie w środowisku zasadowym całkowitą zawartość czterotionianu. Współoznaczanie przeprowadzano w zakresie 30–400 μmoli obydwu związków w próbce z dokładnością 1%.

Tetrathionate can be determined titrimetrically with iodine solution after its prior transformation into thiosulfate in the reaction with sulfite, cyanide or sulfide [1, 2, 3]. These methods can be useful for codetermination of thiosulfate and tetrathionate. Hypochlorite [4], chloramine T [5], periodate [6], cerium (IV) [7, 8], ferricyanide [9] were used as oxidants in the titrimetric determination of tetrathionate. The acidimetric method [10] is based on the titration of hydrogen ions formed in the reaction of tetrathionate with mercuric chloride. The induced iodine–azide reaction [11] was applied in simultaneous determination of tetrathionate and thiosulfate. Tetrathionate and its mixtures with thiosulfate were also determined spectrophotometrically [12–14].

The determination of tetrathionate based on its prior transformation into thiosulfate and sulfite in NaOH medium according to the following reaction:

$$2S_4O_6^{2-} + 6OH^- \rightarrow 3S_2O_3^{2-} + 2SO_3^{2-} + 3H_2O \quad (1)$$

and the iodimetric titration in alkaline medium of the sum of products of the above reaction is presented in this paper.

In order to simultaneously determine thiosulfate and tetrathionate we used the well-known reaction of thiosulfate with iodine in neutral medium, which led to tetrathionate. Tetrathionate, present in the initial sample and that formed in the course of thiosulfate oxidation, was iodimetrically determined in alkaline medium after its transformation into thiosulfate and sulfite.

## EXPERIMENTAL

### Reagents and apparatus

Water doubly distilled in glass apparatus and the following reagents of analytical grade purity: sodium hydroxide, sodium thiosulfate, potassium iodide, iodine were used. A standard tetrathionate solution was obtained by stoichiometric oxidation of thiosulfate solution by an iodine solution. Iodine standard solutions 0.02 mol $l^{-1}$, 0.06 mol $l^{-1}$, 0.12 mol $l^{-1}$ and 0.24 mol $l^{-1}$ were prepared. A pH-meter N–517 (Mera Elwro), with a platinum electrode and saturated calomel electrode and a magnetic stirrer were used.

### Procedures

**1. Potentiometric titration of tetrathionate.** The samples of tetrathionate (10–800 μmol) were added to about 50 ml of the 5 mol $l^{-1}$ solution of sodium hydroxide and titrated with iodine using the potentiometric detection of the end-point with a platinum indicator electrode and a saturated calomel electrode. The optimal time between the introduction of tetrathionate sample to the solution of sodium hydroxide and beginning of the process of titration is 1–10 min. The content of the tested substance was calculated according to the equation:

$$n = \frac{c(\mathrm{I}) \times V}{z} \times 10^3 \quad (2)$$

where:

$n$ content of the determined substance (μmol)

$c$(I) concentration of the titrant (mol $l^{-1}$)

*V* volume of the titrant in the end-point in (ml) and
z = 14, the number of electrons transferred per moleof oxidized substance.

**Simultaneous determination of thiosulfate and tetrathionate.** The sample of the mixture of thiosulfate and tetrathionate was titrated with iodine solution in neutral medium in the presence of starch. The content of thiosulfate ($n_{Na_2S_2O_3}$) was calculated using the formula (1), where z = 1. The volume of 10 mol $l^{-1}$ sodium hydroxide solution was added to the above-mentioned solution, obtained after the titration of thiosulfate in order to reach the concentration 5 mol $l^{-1}$ and a few minutes later the resultant solution was potentiometrically titrated with the iodine solution. The total content of tetrathionate ($\Sigma n_{Na_2S_4O_6}$) was calculated according to the formula (1), where z = 14. The content of tetrathionate in the primary sample was calculated using the following formula:

$$n_{Na_2S_4O_6} = \Sigma n_{Na_2S_4O_6} - \frac{1}{2} n_{Na_2S_2O_3}$$

## RESULTS AND DISCUSSION

The stoichiometry and the reaction rate of tetrathionate dissolution in alkaline medium depend on the concentration of hydroxide [2, 9, 15]. Solymosi and Varga [9] noted, that the tetrathionate dissolution follows the equation (1) in 5 mol $l^{-1}$ NaOH solution during a few minutes.

We found, that iodimetric potentiometric titration of tetrathionate proceeded properly, if the concentration of NaOH was 5 mol $l^{-1}$ and the time between introduction of tetrathionate and beginning of titration was 1–10 min.

**Table 1.** Results of determination of tetrathionate; n = 6

| Taken<br>μmol | Found<br>$\bar{x} \pm t_{0.95} \cdot s/\sqrt{n}$<br>μmol | Relative standard deviation<br>% |
|---|---|---|
| 10.00 | 10.04 ± 0.03 | 0.30 |
| 20.00 | 20.08 ± 0.07 | 0.35 |
| 50.00 | 50.38 ± 0.13 | 0.24 |
| 100.0 | 99.4 ± 0.2 | 0.16 |
| 200.0 | 200.9 ± 0.5 | 0.25 |
| 400.0 | 402.0 ± 0.8 | 0.18 |
| 800.0 | 804.4 ± 1.5 | 0.17 |

In the developed procedure very good results of titration were achieved when the content of tetrathionate in a sample was 10–800 μmol. The results of iodimetric determination of tetrathionate are presented in Table 1 and potentiometric titration curves are shown in Figure 1.

The total reaction between tetrathionate and iodine is given by the following equation:

$$S_4O_6^{2-} + 7I_2 + 20\,OH^- \rightarrow 4SO_4^{2-} + 14I^- + 10H_2O \qquad (2)$$

Thus, the number of electrons transferred per mole of oxidized substance is 14. It is important to remember, that thiosulfate and sulfite which are formed in the reaction (1), are directly oxidized in alkaline medium. It is known that iodimetric potentiometric titration of thiosulfate and sulfite [16] proceeds properly when the concentration of NaOH is higher than 2.4 mol $l^{-1}$. In such strong alkaline solution, during 5–10 min, being the time needed for a titration, the reaction of sulfite with oxygen from the air does not occur. The above-mentioned phenomena can cause negative errors in titration of sulfite in neutral medium.

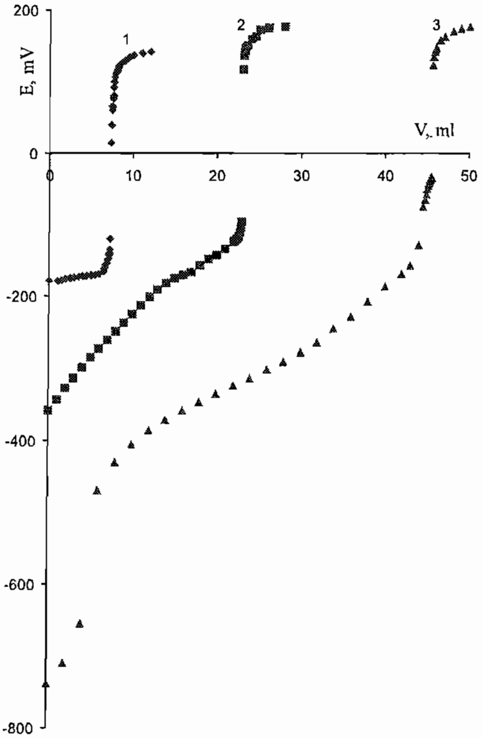

**Figure 1.** The record of potentiometric titration of $Na_2S_4O_6$: (1) 10 mmol with 0.02 mol $l^{-1}$ iodine solution; (2) 100 mmol with 0.06 mol $l^{-1}$ iodine solution; (3) 400 mmol with 0.12 mol $l^{-1}$ solution iodine

This method is useful for accurate and fast simultaneous determination of thiosulfate and tetrathionate in one sample (Table 2). In this analysis the following anions do not interfere: $SO_4^{2-}$, $PO_4^{3-}$, $NO_3^-$, $NO_2^-$, $Cl^-$, $Br^-$, $I^-$, $AsO_4^{3-}$. The following ions: $S^{2-}$, $SO_3^{2-}$, $CN^-$, $SCN^-$, $AsO_3^{3-}$, $S_xO_6^{2-}$ cannot be present in the sample, as they react with iodine.

**Table 2.** Results of simultaneous determination of thiosulfate and tetrathionate; n = 3

| Taken µmol | | Found $\bar{x} \pm t_{0.95} \cdot s/\sqrt{n}$ µmol | | Relative standard deviation % | |
|---|---|---|---|---|---|
| $Na_2S_2O_3$ | $Na_2S_4O_6$ | $Na_2S_2O_3$ | $Na_2S_4O_6$ | $Na_2S_2O_3$ | $Na_2S_4O_6$ |
| 50.00 | 50.00 | 50.24 ± 0.10 | 49.60 ± 0.10 | 0.08 | 0.08 |
| 100.0 | 100.0 | 99.17 ± 0.40 | 99.89 ± 0.90 | 0.18 | 0.38 |
| 100.0 | 50.00 | 99.38 ± 0.80 | 50.25 ± 0.82 | 0.31 | 0.66 |
| 120.0 | 30.00 | 119.9 ± 0.4 | 29.86 ± 0.40 | 0.14 | 0.54 |
| 200.0 | 50.00 | 200.4 ± 1.7 | 50.00 ± 0.87 | 0.34 | 0.70 |
| 400.0 | 50.00 | 398.0 ± 1.7 | 50.20 ± 0.87 | 0.17 | 0.70 |
| 100.0 | 150.0 | 99.77 ± 0.45 | 149.1 ± 0.9 | 0.18 | 0.24 |
| 100.0 | 200.0 | 99.28 ± 0.45 | 198.9 ± 1.3 | 0.18 | 0.26 |
| 100.0 | 400.0 | 99.81 ± 0.42 | 400.9 ± 2.4 | 0.17 | 0.24 |
| 50.00 | 400.0 | 49.76 ± 0.42 | 400.1 ± 6.0 | 0.34 | 0.60 |

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