Analytical Chemistry of Polythionates and Thiosulfate
A Review

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The reaction of hydrogen sulfide with sulfur dioxide in aqueous solution yields Wackenroder's solution, which contains polythionates \( (S_xO_{6x}^-: x=3,4\ and\ 5) \) and thiosulfate. Various reactions of polythionates with such reagents as sulfite, cyanide, sulfide, permanganate and others are reviewed, in which the thiosulfate and/or thiocyanate formed by these reactions of polythionates are measured titrimetrically, spectrophotometrically and coulometrically. As a result, simultaneous equations can be obtained through corresponding different procedures and can be used for the determination of polythionates in their mixtures with other sulfur anions. Furthermore, modern liquid chromatography is described for the separation of polythionates and thiosulfate, in which quite different chromatographic techniques and conditions were employed.

Keywords Wackenroder's solution, polythionates reaction, polythionates mixture analysis, spectrophotometry, polythionates high performance liquid chromatography

1 Introduction

Compounds of composition \( H_xS_{6-x}O_{6-x} \) have been known for a long time in the form of some salts that are rather unstable in aqueous solution. For many years the accepted values for \( x \) have been 3 - 6, though \( x \) varies from 3 to 80.\(^1\) Detailed knowledge of the chemistry of the compounds designated as polythionic acids is still restricted to the first four members. They were found in an aqueous solution of sulfur dioxide and hydrogen sulfide, known as Wackenroder's solution\(^3\) or Samans solution.\(^4\) Polythionic acids can also be designated as disulfonic acids of the sulfanes. This nomenclature would show the fact that the dithionic acid, \( H_2S_2O_6 \), formed by an oxidative treatment of sulfites, has chemically nothing to do with the real polythionic acids, which are reduction products of sulfites. Therefore, dithionate is excluded here. Thiosulfate is reviewed because polythionates are formed as mixtures with thiosulfate. Additionally, polythionates are often converted to thiosulfate by their reactions with some reagents such as cyanide and sulfite, in which the thiosulfate formed is measured for the determination of polythionates. Polythionates had been neglected for many years because of their instability, together with the fact that they are formed in complex mixtures. The determination of individual polythionates in the same solution has long been a tedious, and in many cases impossible task. However, they play important roles in technical processes, environmental chemistry, the sulfur metabolism of certain sulfur bacteria and, generally, in many basic reactions of inorganic sulfur chemistry. Hence, the analytical chemistry of the polythionates is of practical significance to both basic chemistry and industry. In the present review, a comprehensive survey concerning the determination of each polythionate up to hexathionate (tetrasulfanedisulfonate) in both the absence and presence of other sulfur anions is described, including chromatographic separations of polythionate mixtures.
2 Titrimetric Methods

2-1 Thiosulfate

Thiosulfate is oxidized to tetrathionate by iodine according to the following equation:

\[ 2S_2O_3^{2-} + I_2 \rightarrow S_4O_6^{2-} + 2I^- \]  

\( (1) \)

The iodometric method based on this reaction is the simplest and the best method for the determination of thiosulfate, because the above reaction proceeds to stoichiometric completion in an acidic medium. The end-point of the reaction is usually detected visually using a starch solution. Other oxidizing agents such as bromine\(^2\), iodate\(^6\) and manganate\(^7\) have been recommended for the oxidation of thiosulfate. For practical purposes only iodine is of prime importance for the determination of thiosulfate.

2-1-1 Thiosulfate–sulfite or sulfide mixture

The method\(^8\)\(^9\) using formaldehyde gives excellent results for the analysis of thiosulfate–sulfite mixtures. Formaldehyde forms an additional compound with sulfite, which is stable toward iodine. An aliquot of the sample solution is directly titrated with a standard iodine solution and a further aliquot is titrated in the same way after the addition of formaldehyde. The first titration gives the sum of thiosulfate and sulfite; the second gives only the amount of thiosulfate. When thiosulfate and sulfide are present together in a sample solution, sulfide is expelled as \( \text{H}_2\text{S} \) by bubbling the solution with nitrogen gas after the addition of hydrochloric acid; thiosulfate can then be determined iodometrically. In a second sample both anions are titrated iodometrically.

2-1-2 Thiosulfate–sulfide–sulfite mixture

Kurtenacker and Wollak\(^10\) have proposed an iodometric titration method for the determination of thiosulfate, sulfide and sulfite in a mixture, which has been extensively employed in the past. According to this method, the total amounts of these three ions are titrated iodometrically in one aliquot. After precipitation and filtration of zinc or cadmium sulfide, the sum of thiosulfate and sulfite can be titrated in one aliquot of the filtrate. To another aliquot of the filtrate, formaldehyde is added in order to mask the sulfite, and the thiosulfate is determined iodometrically. A potential difficulty here is the coprecipitation of thiosulfate and sulfite on the bulky zinc or cadmium sulfide precipitate. A precipitate of smaller surface area, and therefore causing less coprecipitation, is produced by adding a fresh suspension of zinc or cadmium carbonate hydroxide. Wiele\(^11\) also proposed an iodometric method for the analysis of a thiosulfate–sulfide–sulfite mixture in magnesium or calcium carbonate. In one aliquot sample the total amounts of three sulfur species are determined by iodometric titration in an acid medium. In a new sample the sulfur dioxide (\( \text{SO}_2 \)) from the sulfite is determined after distillation in the presence of mercury(II) chloride from hydrochloric acid medium. In a third sample the thiosulfate is determined by iodometric titration in the presence of cadmium acetate and formaldehyde.

On the other hand, Ikeda and Satake\(^12\) have developed a method for a successive determination of thiosulfate, sulfide and sulfite by potentiometric titration using a silver–silver sulfide electrode for sulfide and a silver–silver iodide electrode for thiosulfate and sulfite as the indicator electrodes. Both the sulfide and thiosulfate are titrated directly with a standard solution of silver nitrate, whereas sulfite is determined by titrating the iodide generated from the reaction of the sulfite with the added iodine. These three sulfur species in their mixtures can be determined directly by the three successive argentometric titrations without any separation procedure.

Thiosulfate was also determined in a mixture containing sulfide, dithionite and sulfite by iodometric titration.\(^13\) The sample solution was first added to a suspension of freshly precipitated zinc carbonate. The zinc sulfide precipitate formed was filtered off and the filtrate was allowed to react with iodine in an acetic acid–acetate buffer solution; both dithionite and sulfite are oxidized to sulfite, whereas thiosulfate to tetrathionate. Then sulfite is added (a) to remove the unreacted iodine and (b) to sulfitolyze the tetrathionate formed. After masking the excess sulfite by formaldehyde, the thiosulfate formed by sulfitolyis of the tetrathionate is titrated with standard iodine. The number of mmol of thiosulfate originally present is given by four times the mmol of iodine used.

2-2 Polythionates in mixtures

Individual polythionates are very similar in their chemical and physical properties. Therefore, a direct determination of a polythionate in mixtures with other polythionates is not practicable. A large number of procedure equations which can be obtained through corresponding different procedures are necessary for the determination of each polythionate in mixtures.

2-2-1 Total polythionates in mixtures

Polythionates (\( \text{S}_x\text{O}_y^{2-}: \ x=3, 4 \) and 5) react with mercury(II) chloride to form \( 4 \) mol of hydronium ions which can be determined alkalinometrically.\(^14\) The stoichiometric equation is as follows:

\[
2\text{S}_x\text{O}_y^{2-} + 3\text{HgCl}_2 + 4\text{H}_2\text{O} \rightarrow \text{HgCl}_2\cdot 2\text{H}_2\text{S} + 8\text{H}^+ + 4\text{Cl}^- + 4\text{SO}_4^{2-} + (2x-6)\text{S}.
\]

\( (2) \)

A reaction of hexathionate with mercury(II) chloride has not yet been investigated. The proposed method is readily applicable to various samples, and is not affected by the presence of weak acids.

A titrimetric method\(^15\) has been described for the determination of various forms of sulfur, in order to distinguish between non-oxidizable sulfate and the oxidizable thio salts including thiosulfate, dithionate,
tri- and tetrathionate. Metal ions are removed, after an oxidizing step, by a cation-exchange resin, and the sulfate is precipitated with a known excess of barium chloride. The excess of barium is back-titrated with a standard EDTA solution. The method consists of determining: (a) the initial sulfate plus the sulfate obtained by oxidizing sulfite with iodine, (b) the total sulfate obtained by oxidizing the polythionates (including the tetrathionate produced by oxidation of thiosulfate by iodine) with acidic hydrogen peroxide, and (c) the total sulfate obtained by oxidation of all thio salts including dithionate with a mixture of hydrogen peroxide, potassium chlorate and concentrated nitric acid. This method is suitable for monitoring mining effluents for the total content of thio salts rather than the individual species.

2 Individual polythionates in mixtures

Goehring et al. have reported an iodimetric method for the determination of individual polythionates in mixtures of trithionate to hexathionate, in which the mixtures were treated in separate aliquots with sulfite, cyanide, sulfide and alkali. The thiosulfate produced is then titrated iodimetrically. The reactions of polythionates with sulfite, cyanide, sulfide and alkali are as follows:

\[ S_xO_6^{2-} + (x-3)SO_3^{2-} \rightarrow S_3O_6^{2-} + (x-3)S_2O_3^{2-} \]  
\( x = 4, 5 \) and 6  
(3)

\[ S_xO_6^{2-} + (x-1)CN^- + H_2O \rightarrow SO_4^{2-} + (x-3)SCN^- + 2HCN + S_2O_3^{2-} \]  
\( x = 4, 5 \) and 6  
(4)

\[ S_xO_6^{2-} + S^2 \rightarrow (x-3)S + 2S_2O_3^{2-} \]  
\( x = 3, 4 \) and 5  
(5)

These reactions were not all investigated in detail. Therefore, the method described by Goehring et al. gave serious errors with a recovery of 56 - 140%.

3 Thiosulfate

3.1 Spectrophotometry

Ozawa has proposed an excellent method for the determination of thiosulfate, which has been extensively employed for the determination of polythionates. When an acid is added to a mixture solution of iodate and excess iodide, the iodine equivalent to the iodate is produced according to the following equation:

\[ IO_3^- + 8I^- + 6H^+ \rightarrow I_3^- + 3H_2O. \]  
(8)

Thus, a standard iodine solution can be readily prepared whenever needed. A molar absorptivity of triiodide at 350 nm is much higher than that of iodine in carbon tetrachloride at 515 nm. Hence, thiosulfate can be determined sensitively by measuring the absorbance of excess iodine (as triiodide) for the reaction of Eq. (1) at 350 nm.

Thiosulfate reacts with cyanide in the presence of copper(II) to form thiocyanate according to

\[ S_2O_3^{2-} + CN^- \rightarrow SO_4^{2-} + SCN^- \]  
(9)

in which the thiocyanate can be determined photometrically as the iron(III)-thiocyanate complex at 460 nm. A further investigation by Nor and Tabatabai indicated that thiosulfate and tetrathionate can be determined in the presence of very large amounts of sulfate. Optimal conditions established for stoichiometric conversion of thiosulfate into thiocyanate have been used for the determination of two species of polythionates in their mixtures. The sensitivity for the determination of thiosulfate could be increased by about 60-fold by extracting the ion-pair formed between the cation of Methylene Blue (MB) and the anion of thiocyanate formed from the thiosulfate. Lanthanum(III) and gold(III) have also been found to catalyze the reaction of thiosulfate with cyanide, and the optimum conditions for quantitative lanthanum(III)-catalyzed cyanolysis of thiosulfate have been established. Thiosulfate was found to react with mercury(II) thiocyanate to yield thiocyanate; this reaction was clarified with special reference to the determination of thiosulfate, in which the thiocyanate formed is photometrically measured. The reaction

\[ 4S_2O_3^{2-} + 6Hg(SCN)_2 + HPO_4^{2-} + 16H_2O \rightarrow Hg_6S_4(OH)_2HPO_4 + 4SO_4^{2-} + 10H_3O^+ + 12SCN^- \]  
(10)

proved to proceed to stoichiometric completion under certain conditions.

3.1.1 Thiosulfate-sulfide-sulfite mixture

Particularly when thiosulfate, sulfide and sulfite are mixed with one another in solution, the identification and determination of these sulfur species are difficult, because they are labile and participate in complex equilibria with the other sulfur compounds formed by their auto-redox reactions. A method has been proposed for the analysis of this mixture, which is based on their oxidation with iodine after proper chemical treatments, followed by a measurement of any excess iodine at 350 nm. In this study, the conditions of stabilization of sulfide and sulfite mixed with each other have been investigated in order to avoid any time-dependent change in the chemical composition of the sample solution containing soluble sulfide, sulfite and thiosulfate. These three sulfur species in their mixture give the following equivalents in three procedures (1 - III) used.
[S₂O₃²⁻]=(S₂O₃²⁻)+2[S²⁻]+2[SO₃²⁻],
[S₂O₃²⁻]₀=[S₂O₃²⁻]+2[S²⁻],
and
[S₂O₃²⁻]ₘ=[S₂O₃²⁻].

The absorbance obtained by procedure I corresponds to the sum of the amount of thiosulfate, twice that of sulfide and twice that of sulfite in the mixture. The absorbance obtained by procedure II, where sulfite was masked by formaldehyde, corresponds to the sum of the amount of thiosulfate and twice that of sulfide. The absorbance obtained by procedure III corresponds only to the amount of thiosulfate, because sulfite was masked by formaldehyde and sulfide was eliminated with the suspension of zinc carbonate hydroxide. The following equations can thus be obtained: [S₂O₃²⁻]=III, [S²⁻]=(II−III)/2 and [SO₃²⁻]=(I−II)/2. Here, I, II and III denote the molar concentrations of thiosulfate, determined using the absorbance obtained by procedures I, II and III, respectively. The proposed method is applicable to the determination of the three sulfur species mixed in amounts of more than 0.05 µmol and gave a relative standard deviation of 3% at 0.4 µmol level. This method was applied to the determination of thiosulfate, sulfide and sulfite in various amounts in fumarolic condensate samples.

3.2 Catalytic methods
The catalytic effect of thiosulfate, sulfide and thiocyanate on the azide-iodine reaction,

2N₃⁻+I₂ → 3N₂+2I⁻,

has been well known. Michalski and Wtorkowska have reported a catalytic method for the determination of ultramicro amounts of thiosulfate, in which amperometry using a rotating platinum electrode was used to follow the reaction rate. Utsumi and Okutani employed the same reaction for the determination of thiosulfate in the range 0.001–0.15 ppm; in this case the excess iodine (as triiodide) was spectrophotometrically measured at 350 nm. Iron(III), copper(II), sulfite and cyanide interfere.

3.3 Electroanalytical methods
There is a need for secondary coulometric titration of thiosulfate since it reacts completely, rapidly and stoichiometrically with iodine. This requirement was met by the addition of excess iodide with a subsequent titration of the electrolytically generated iodine by thiosulfate; the end point was determined by amperometry. This coulometric procedure has been extended to the determination of polythionates, in which the thiosulfate produced from the polythionates was coulometrically titrated.

Recently, a method for the determination of thiosulfate in the range 0.045–0.9 ppm using an iodide ion selective electrode has been proposed. Aqueous thiosulfate was shaken with a solution of iodine in carbon tetrachloride. The organic phase was separated, the excess of iodine extracted into an aqueous sulfite solution and the iodide liberated measured with an iodide-selective electrode. The measured potential was converted directly to the concentration of iodide using two iodide standards approximating the concentration of the unknown. It was possible to determine thiosulfate in various concentration ranges by changing only the concentration of the standard iodine in a carbon tetrachloride solution. For example, this method is applicable to the determination of thiosulfate in the concentration range 4×10⁻³–8×10⁻⁴ M when a 10-ml aliquot of 1×10⁻³ M iodine in carbon tetrachloride is used under the conditions specified in procedure, and in the concentration range 4×10⁻⁷–8×10⁻⁸ M when a 10-ml aliquot of 1×10⁻⁴ M iodine in carbon tetrachloride is used. A linear calibration graph was obtained over any concentration ranges, and thiosulfate was selectively determined, even in the presence of sulfite and sulfide in 100-fold amounts. The proposed method can be expected to be used for the determination of polythionates at the 10⁻⁶ M level.

4 Pure Individual Polythionates

The identification and determination of polythionates in their mixtures are difficult owing to similarities in their chemical and physical properties. Hence, various reactions of individual polythionates should be investigated in detail in order to determine a specific polythionate in the presence of other polythionates. In addition, it is desirable to establish, if possible, the conditions under which all the polythionates concerned are simultaneously and stoichiometrically converted to thiosulfate and/or thiocyanate. There are many difficulties in the analysis of polythionate mixtures, but the determination of individual polythionates in pure form is relatively easy.

4.1 Spectrophotometry
Many investigations have been carried out on the sulfitolysis [Eq. (3)], cyanolysis [Eq. (4)], sulfidolysis [Eq. (5)] and alkalinoysis [Eq. (7)] of polythionates for the determination of polythionates, in which the thiocyanate and/or thiosulfate produced from the polythionates were spectrophotometrically measured.

4.1.1 Cyanolysis
Nietzel and DeSesa employed the cyanolysis reaction for the determination of tetrathionate, in which the thiocyanate formed was photometrically measured as the iron(III)-thiocyanate complex at 460 nm. They pointed out that their method might be suitable for pentathionate and hexathionate, because the higher polythionates react more easily with cyanide to form thiocyanate. However, both of penta- and hexathionate were found not to be stoichiometrically converted to thiocyanate under the conditions of the Nietzel-
DeSesa's method, owing to the partial alkaline decomposition. The reactions of pentathionate\(^{35}\) and hexathionate\(^{36}\) with cyanide have been investigated in detail and the conditions for the cyanolysis of penta- and hexathionate to go well to stoichiometric completion have been established. The optimum pH ranges for the cyanolysis of penta- and hexathionate are, respectively, 8.0 – 8.8 and 7.8 – 8.9 when cyanolyzed for 30 min at 40°C. On the other hand, tetrathionate\(^{37}\) proved to be completely converted to thiocyanate over the pH range 8.3 – 12.1 under the same conditions as those for both penta- and hexathionate. Hence, when these three polythionates were cyanolyzed in the solution buffered to the pH range 8.3 – 12.1 under the same conditions as those for both penta- and hexathionate. Hence, when these three polythionates were cyanolyzed in the solution buffered to the pH range 8.3 – 8.8 for 30 min at 40°C, the calibration graphs obtained for tetra-, penta- and hexathionate were, as can be seen in Fig. 1, in good agreement with one another, respectively, in which the molar concentration scales for penta- and hexathionate were drawn to twice and three times the concentration scale for tetrathionate. This indicates that all three of these polythionates could be completely converted to thiocyanate according to Eq. (4) under the identical conditions. In addition, it was shown that the sensitivity for the determination of polythionates (S\(_6\)O\(_{15}\)^\(-\): x=4, 5 and 6) can be increased approximately 60-fold by extracting the thiocyanate formed as an ion pair with Methylene Blue into an organic solvent.\(^{38}\) The optimal pH ranges for the cyanolysis of polythionates at the 10\(^{-6}\) M level were, respectively, 7.2 – 10.8 for tetrathionate and 7.2 – 7.6 for both penta- and hexathionate when cyanolyzed at 40°C for 4.5 h. The calibration graphs obtained for tetra-, penta- and hexathionate in the solutions buffered to pH range 7.2 – 7.6 are, respectively, once, twice and three times as sensitive as that for thiocyanate when plotted as molar concentrations (Fig. 2). This proves that all three polythionates can be quantitatively converted to thiocyanate, even at the 10\(^{-6}\) M level, according to Eq. (4).

Urban\(^{39}\) and Kelly\(^{40}\) investigated the cyanolysis of trithionate and utilized this reaction for the determination of trithionate. Urban's method has the disadvantage of requiring 16 h for the cyanolysis at room temperature; even then, the cyanolysis was not quantitative. Kelly attempted to complete the cyanolysis of trithionate as fast as possible; the cyanolysis was carried out at pH 9.6 for 45 min at a temperature of boiling water. Under these conditions, only 87% of trithionate was converted into thiocyanate and the rest into thiosulfate. Accordingly, these methods can not be considered accurate. Lanthanum(III)\(^{41}\) has been found to have a catalytic effect on the conversion of trithionate into thiocyanate, and a rapid and accurate method for the determination of trithionate has been developed. This method is based on the formation of thiocyanate equivalent to trithionate in the presence of lanthanum(III) according to

\[
\text{S}_3\text{O}_6^2^- + 3\text{CN}^- + \text{H}_2\text{O} \rightarrow \text{S}_2\text{O}_3^- + \text{S}_4\text{O}_6^2^- + 2\text{HCN} + \text{SCN}^-.
\]  

and on the photometric measurement of the thiocyanate thus formed as the iron(III)-thiocyanate complex at 460 nm. Complete cyanolysis was obtained in 20 min at 10°C over the pH range 9.3 – 9.6.

4-1-2 Sulfitolysis and sulfidolysis

Iwasaki and Suzuki\(^{42}\) proposed a method for the determination of tetrathionate which is based on the sulfitolysis of tetrathionate [Eq. (3)], followed by a photometric measurement of any excess iodine (as triiodide) for the thiosulfate formed at 350 nm. Pentathionate\(^{43}\) and hexathionate\(^{44}\) were stoichiomet-
rically converted to thiosulfate in the pH ranges 6.5 - 8.2 and 6.9 - 9.5, respectively, when sulfitolyzed for 20 min at room temperature. The sulfitolysis of tetrathionate was further investigated in detail and tetrathionate proved to be completely converted into thiosulfate over the pH range 7.7 - 12.5 under the same conditions as those for both penta- and hexathionate. Therefore, the optimal pH range for all three of these polythionates was found to be 7.7 - 8.2 when sulfitolyzed for 20 min at room temperature. The calibration graphs obtained for tetra-, penta- and hexathionate were, as can be seen in Fig. 3, respectively, in good agreement with one another when plotted in terms of equivalent concentrations.

Koh et al. investigated the sulfidolysis of polythionates in detail and proposed methods for the determination of tetra- and pentathionate which are based on the formation of thiosulfate equivalent to the polythionates, followed by a measurement of the excess iodine (triiodide) for the thiosulfate formed. The conditions under which tetra- and pentathionate are stoichiometrically converted into thiosulfate according to Eq. (5) were established by varying the reaction time, pH and amount of sulfide. The excess of sulfide used for the sulfidolysis of the polythionates was removed with a suspension of freshly precipitated zinc carbonate hydroxide. The polysulfide formed by the reaction of sulfide with the free sulfur produced by the sulfidolysis of polythionates might readily undergo air-oxidation to form thiosulfate at both higher temperatures and higher pH levels. Tetrathionate was completely converted to thiosulfate according to Eq. (5) over the pH range of 7.0 - 9.5 when allowed to react with sulfide at 10°C for 20 min. On the other hand, pentathionate was quantitatively converted into thiosulfate over the pH range 5.1 - 7.0 when sulfidolyzed at 20°C for 10 min. There was no need for pentathionate to be sulfidolyzed at lower temperatures, such as 10°C, because the optimum pH for the stoichiometric sulfidolysis is lower than that for tetrathionate.

4.1.3 Other reactions

It has been stated that tetrathionate reacts with hydroxide according to Eq. (13) in a weak alkaline medium and according to Eq. (14) in a strong alkaline solution:

$$4S_4O_6^{2-} + 6OH^- \rightarrow 5S_2O_3^{2-} + 2S_2O_5^{2-} + 3H_2O \quad (13)$$
$$2S_4O_6^{2-} + 6OH^- \rightarrow (2x - 5)S_2O_3^{2-} + (10 - 2x)SO_3^{2-} + 3H_2O \quad (x = 3, 4 \text{ and } 5). \quad (14)$$

Miura and Koh proposed methods for the determination of tetrathionate and pentathionate, in which the excess iodine for the thiosulfate formed by the reaction of the polythionates with hydroxide was photometrically measured as triiodide at 350 nm. It was impossible to find the conditions under which the reaction of the polythionates with hydroxide proceeds according to Eq. (13) or (14); both tetra- and pentathionate were found to be converted not only to thiosulfate and sulfite, but also to sulfide. Under the optimum conditions for pentathionate in which 2 mol of thiosulfate are produced from 1 mol of pentathionate, the reaction of tetrathionate with hydroxide proceeded according to the following equation:

$$10S_4O_6^{2-} + 34OH^- \rightarrow 13S_2O_3^{2-} + 38SO_3^{2-} + 4/3S_2S + 17H_2O. \quad (15)$$

Recently, sensitive methods for pentathionate and hexathionate have been published. The procedure involves oxidation of the polythionates with a given amount of permanganate in sulfuric acid medium, followed by spectrophotometric determination of the triiodide formed by the oxidation of iodide with an excess of permanganate. The analytical conditions were established by varying the temperature, reaction time and amounts of sulfuric acid and permanganate. It has been confirmed that under the identical conditions, each 2 mol of pentathionate and hexathionate react completely with 7 and 9 mol of permanganate, respectively. The proposed method is applicable to the determination of pentathionate in the range $2 \times 10^{-7} - 1.4 \times 10^{-5}$ M and hexathionate in the range $1.8 \times 10^{-7} - 1.1 \times 10^{-5}$ M.

Trithionate was found to react with mercury(II) thiocyanate to yield thiocyanate according to the following equation:

$$4S_3O_6^{2-} + 6Hg(SCN)_2 + HPO_4^{2-} + 28H_2O \rightarrow Hg_6S_4(OH)_2HPO_4 + 8SO_4^{2-} + 18H_3O^+ + 12SCN^- . \quad (16)$$

A detailed examination of this reaction led to the
determine individual polythionates in their mixtures by solving the simultaneous equations which can be obtained through corresponding different procedures. Since various decomposition reactions of polythionates such as cyanolysis, sulfitolysis and sulfidolysis have been investigated in detail, it is possible to determine individual polythionates in their mixtures by solving the simultaneous equations which can be obtained through corresponding different procedures.

5 Polythionates and Other Sulfur Anions in Mixtures

5.1 Spectrophotometry

Since various decomposition reactions of polythionates such as cyanolysis, sulfitolysis and sulfidolysis have been investigated in detail, it is possible to determine individual polythionates in their mixtures by solving the simultaneous equations which can be obtained through corresponding different procedures. However, the determination of tetrathionate by its cyanolysis.

The proposed method for two-species of polythionates in their mixtures consists in a determination of different amounts of the thiocyanate formed according to Eqs. (4) and (19) on two 10-ml aliquots of sample solution containing two polythionates; one is treated by procedure I and the other by procedure II. For the tetrathionate–pentathionate mixture, the two species of the polythionates give the following equivalents in the two procedures:

\[ [SCN^-]_I = [S_xO_{62-}] + 2[S_yO_{2-}] \]

and

\[ [SCN^-]_II = [2[S_xO_{62-}] + 3[S_yO_{2-}] \]

Hence, the following equations can be obtained: \([S_xO_{2-}] = 2II - 3I \) and \([S_yO_{2-}] = 2II - II \). Here, I and II denote the molar concentrations of thiocyanate determined by procedures I and II, respectively. Similarly, for the tetrathionate–hexathionate mixture \([S_xO_{2-}] = (3II - 4I)/2 \) and \([S_yO_{2-}] = (2II - II)/2 \), and for the pentathionate-hexathionate mixture \([S_xO_{2-}] = 3II - 4I \) and \([S_yO_{2-}] = 3II - 2II \). By using these equations, tetrathionate–pentathionate, tetrathionate–hexathionate and pentathionate–hexathionate mixtures can be analyzed. The sensitivity for the determination of two species of polythionates in their mixtures could be increased about 60-fold by extracting the thiocyanate formed into an organic solvent as an ion pair with Methylene Blue. The proposed method is suitable for the determination of polythionates at the \(10^{-7} - 10^{-6} \) M level and is more sensitive than any photometric method. The values of x in the formula, \(S_xO_{2-}\), for aqueous polythionates have been evaluated by the determination of different amounts of the thiocyanate formed according to Eqs. (4) and (19). Suppose that I and II denote the molar concentrations of thiocyanate determined by the respective procedures I and II. Then, 

\[ 1/II = (x-3)/(x-2) \]

where x is the number of sulfur atoms in the formula for \(S_xO_{2-}\). When arranged with respect to x, the equation \(x = 1/(II-1) - 3\) can be obtained. By using this equation, values of x were developed as an accurate method for the determination of trithionate, in which the thiocyanate liberated is photometrically measured as the iron(III)-thiocyanate complex at 460 nm. The optimum conditions under which the reaction of trithionate proceeds to stoichiometric completion according to Eq. (16) have been established with special reference to the determination of trithionate.

4.2 Electroanalytical methods

Tetrathionate is reducible at the dropping-mercury electrode. In a supporting electrolyte solution of potassium nitrate, the polarogram showed the peak of a pronounced polarographic maximum. This peak could be suppressed by the addition of gelatin or certain dyes, but quinoline and acridine are especially suitable as maximum suppressors. For the determination of tetrathionate, polarograms were best recorded in M solutions of phosphoric acid or of the ammonium phosphate at pH range 9.35 – 8.15 and with 0.001% quinoline. The half-wave potential is independent of the pH value of 1 M phosphate supporting electrolyte, but it becomes more negative as the concentration of tetrathionate increases. The proposed method is applicable to the determination of tetrathionate in the presence of dithionate, trithionate, sulfite or thiosulfate, but pentathionate interferes.

Murayama reported a polarography for tri- and tetrathionate in a supporting electrolyte solution of potassium chloride or calcium chloride. The reduction of tri- and tetrathionate at the dropping-mercury electrode is irreversible and considered to be as follows:

\[ S_yO_{2-} + xCN^- + H_2O \rightarrow SO_4^{2-} + (x-2)SCN^- + 2HCN + SO_3^{2-}. \]

\[ (x=4, 5 \text{ and } 6) \]

The optimal copper(II)-catalyzed cyanolysis conditions of the thiosulfate formed from the polythionates have been established by adding copper(II) to the reaction mixture in which the reaction of Eq. (4) was completed. Accordingly the overall reaction is as follows:

\[ S_yO_{2-} + xCN^- + H_2O \rightarrow SO_4^{2-} + (x-2)SCN^- + 2HCN + SO_3^{2-}. \]

\[ (x=4, 5 \text{ and } 6) \]

The proposed method for two-species of polythionates in their mixtures consists in a determination of different amounts of the thiocyanate formed according to Eqs. (4) and (19) on two 10-ml aliquots of sample solution containing two polythionates; one is treated by procedure I and the other by procedure II. For the tetrathionate–pentathionate mixture, the two species of the polythionates give the following equivalents in the two procedures:

\[ [SCN^-]_I = [S_xO_{62-}] + 2[S_yO_{2-}] \]

and

\[ [SCN^-]_II = [2[S_xO_{62-}] + 3[S_yO_{2-}] \]

Hence, the following equations can be obtained: \([S_xO_{2-}] = 2II - 3I \) and \([S_yO_{2-}] = 2II - II \). Here, I and II denote the molar concentrations of thiocyanate determined by procedures I and II, respectively. Similarly, for the tetrathionate–hexathionate mixture \([S_xO_{2-}] = (3II - 4I)/2 \) and \([S_yO_{2-}] = (2II - II)/2 \), and for the pentathionate-hexathionate mixture \([S_xO_{2-}] = 3II - 4I \) and \([S_yO_{2-}] = 3II - 2II \). By using these equations, tetrathionate–pentathionate, tetrathionate–hexathionate and pentathionate–hexathionate mixtures can be analyzed. The sensitivity for the determination of two species of polythionates in their mixtures could be increased about 60-fold by extracting the thiocyanate formed into an organic solvent as an ion pair with Methylene Blue. The proposed method is suitable for the determination of polythionates at the \(10^{-7} - 10^{-6} \) M level and is more sensitive than any photometric method. The values of x in the formula, \(S_xO_{2-}\), for aqueous polythionates have been evaluated by the determination of different amounts of the thiocyanate formed according to Eqs. (4) and (19). Suppose that I and II denote the molar concentrations of thiocyanate determined by the respective procedures I and II. Then, 

\[ 1/II = (x-3)/(x-2) \]

where x is the number of sulfur atoms in the formula for \(S_xO_{2-}\). When arranged with respect to x, the equation \(x = 1/(II-1) - 3\) can be obtained. By using this equation, values of x were determined.
determined for aqueous solutions of pure polythionates. The results are shown in Table 1. Urban deduced that aqueous polythionates, with the exception of tetrathionate, are present as mixtures containing other polythionates from tetrathionate upwards. However, his conclusion is not acceptable; the lower values of \( x \) obtained under Urban's conditions were caused by a partial alkaline decomposition of the polythionates accompanied with hydrolysis of the cyanide used. Table I shows that tetra-, penta- and hexathionate, respectively, are present as pure polythionates even at \( 10^{-6} \) M levels.

5.2 Total polythionates (\( S_xO_6^{2-} \): \( x=4, 5 \) and 6)-thiosulfate-sulfite mixture

When polythionates undergo cyanolysis, the reaction of Eq. (4) proceeds to stoichiometric completion; each 1 mol of the polythionates produces 1 mol of thiosulfate. Total polythionates (tetra-, penta- and hexathionate) were determined by photometrically measuring the excess iodine for the thiosulfate formed from the polythionates after masking the excess of cyanide with formaldehyde. Total polythionates, thiosulfate and sulfite in a mixture give the following equivalents in three procedures:

\[
[S_2O_3^{2-}]_I = [S_4O_6^{2-}] + [S_2O_3^{2-}], \\
[S_2O_3^{2-}]_{II} = [S_2O_3^{2-}], \\
[S_2O_3^{2-}]_{III} = [S_2O_3^{2-}] + 2[SO_3^{2-}].
\]

The absorbance obtained by procedure I corresponds to the sum of the amount of tetrathionate and that of thiosulfate in the mixture, because the sulfite in the mixture was masked by the formaldehyde added for removing the excess sulfite. The absorbance obtained by procedure II, in which sulfitolysis of tetrathionate was not carried out, corresponds to the amount of thiosulfate in the mixture. The absorbance obtained by procedure III corresponds to the sum of the amount of thiosulfate and twice that of sulfite in the mixture. Hence, the following equations can be derived: [\( S_2O_3^{2-} \)]_I = [\( S_4O_6^{2-} \)] + [\( S_2O_3^{2-} \)], [\( S_2O_3^{2-} \)]_{II} = [\( S_2O_3^{2-} \)], and [\( S_2O_3^{2-} \)]_{III} = [\( S_2O_3^{2-} \)] + 2[\( SO_3^{2-} \)].

The absorbance obtained by procedure I corresponds to the sum of the amount of tetrathionate and that of thiosulfate in the mixture, because the sulfite in the mixture was masked by the formaldehyde added for removing the excess sulfite. The absorbance obtained by procedure II, where cyanolysis of polythionates was not carried out and the sulfite in the mixture was masked with formaldehyde, corresponds only to the amount of thiosulfate in the mixture. The absorbance obtained by procedure III, where polythionates were not cyanolyzed, corresponds to the sum of the amount of thiosulfate and twice that of sulfite in the mixture. The following equations can therefore be obtained: [\( S_2O_3^{2-} \)] = [\( S_4O_6^{2-} \)] + 2[\( SO_3^{2-} \)].

The absorbance obtained by procedure I corresponds to the sum of the amount of tetrathionate and that of thiosulfate in the mixture, because the sulfite in the mixture was masked by the formaldehyde added for removing the excess sulfite. The absorbance obtained by procedure II, where cyanolysis of tetrathionate was not carried out, corresponds to the amount of thiosulfate in the mixture. The absorbance obtained by procedure III corresponds to the sum of the amount of thiosulfate and twice that of sulfite in the mixture. Hence, the following equations can be derived: [\( S_2O_3^{2-} \)] = [\( S_4O_6^{2-} \)] + [\( S_2O_3^{2-} \)], [\( S_2O_3^{2-} \)]_{II} = [\( S_2O_3^{2-} \)], and [\( S_2O_3^{2-} \)]_{III} = [\( S_2O_3^{2-} \)] + 2[\( SO_3^{2-} \)].

The absorbance obtained by procedure I corresponds to the sum of the amount of tetrathionate and that of thiosulfate in the mixture, because the sulfite in the mixture was masked by the formaldehyde added for removing the excess sulfite. The absorbance obtained by procedure II, where cyanolysis of polythionates was not carried out and the sulfite in the mixture was masked with formaldehyde, corresponds only to the amount of thiosulfate in the mixture. The absorbance obtained by procedure III, where polythionates were not cyanolyzed, corresponds to the sum of the amount of thiosulfate and twice that of sulfite in the mixture. The following equations can therefore be obtained: [\( S_2O_3^{2-} \)] = [\( S_4O_6^{2-} \)] + 2[\( SO_3^{2-} \)].

The absorbance obtained by procedure I corresponds to the sum of the amount of tetrathionate and that of thiosulfate in the mixture, because the sulfite in the mixture was masked by the formaldehyde added for removing the excess sulfite. The absorbance obtained by procedure II, where cyanolysis of tetrathionate was not carried out, corresponds to the amount of thiosulfate in the mixture. The absorbance obtained by procedure III corresponds to the sum of the amount of thiosulfate and twice that of sulfite in the mixture. Hence, the following equations can be derived: [\( S_2O_3^{2-} \)] = [\( S_4O_6^{2-} \)] + [\( S_2O_3^{2-} \)], [\( S_2O_3^{2-} \)]_{II} = [\( S_2O_3^{2-} \)], and [\( S_2O_3^{2-} \)]_{III} = [\( S_2O_3^{2-} \)] + 2[\( SO_3^{2-} \)].

As can be seen in Fig. 3, the calibration graphs for tetra-, penta- and hexathionate, obtained under the identical procedure, were in good agreement with one another, respectively. Hence, the sulfitolysis of polythionates has played, and will play further, a critical role in the development of methods for the analysis of mixtures of the polythionates.

5.1.4 Polythionate (\( S_xO_6^{2-} \): \( x=4 \) or 5)-thiosulfate-sulfide mixture

The mixture of tetrathionate (or pentathionate), thiosulfate and sulfide was analyzed by using sulfitolysis of the polythionates. For the tetrathionate-thiosulfate-sulfide mixture, these three sulfur species...
The absorbance obtained by procedure I corresponds to the sum of the amount of thiosulfate and twice that of tetrathionate in the mixture, the sulfide in the mixture being removed by the zinc carbonate hydroxide suspension. The absorbance obtained by procedure II, in which the sulfidolysis of tetrathionate was not carried out, corresponds only to the amount of thiosulfate in the mixture. The absorbance obtained by procedure III corresponds to the sum of the amount of thiosulfate and twice that of sulfide in the mixture. Hence, the following equations can be obtained: 

\[ [S_{2}O_{3}^{2-}] = (I-II)/2, \]
\[ [S_{2}O_{3}^{2-}] = II \text{ and } [S^{2-}] = (III-II)/2, \]

where I, II and III denote the molar concentrations of thiosulfate, determined using the absorbance obtained by procedures I, II and III, respectively. Similarly, for the pentathionate-thiosulfate-sulfide mixture, the thiocyanate formed under procedure IV are measured spectrophotometrically after proper chemical treatments. These four sulfur compounds in their mixture give the following equivalents in the four procedures:

\[ [S_{2}O_{3}^{2-}] = [S_{4}O_{6}^{2-}] + [S_{2}O_{3}^{2-}], \]
\[ [S_{2}O_{3}^{2-}] = [S_{4}O_{6}^{2-}] + [S_{2}O_{3}^{2-}], \]
\[ [S_{2}O_{3}^{2-}] = [S_{4}O_{6}^{2-}] + 2[S^{2-}]. \]

The optimum conditions for the sulfidolysis of tetrathionate is different from those for pentathionate. In addition sulfidolysis of hexathionate has not yet been investigated. It is desirable for the conditions, under which all three polythionates of tetra-, penta- and hexathionate are simultaneously and stoichiometrically converted into thiocyanate according to Eq. (5), to be established, for the analysis of mixtures of various polythionates.

5-1-5 Thiosulfate-trithionate-tetrathionate mixture

Kelly et al. have proposed a method for the determination of thiosulfate, trithionate and tetrathionate in a mixture using their cyanolysis. This method consists in the determination of different amounts of the thiocyanate formed by three procedures on three 10-ml aliquots containing thiosulfate, trithionate and tetrathionate. These three sulfur compounds in their mixture give the following equivalents in the three procedures:

\[ [SCN^{-}] = [S_{4}O_{6}^{2-}], \]
\[ [SCN^{-}] = 2[S_{2}O_{3}^{2-}] + [S_{2}O_{3}^{2-}], \]

and

\[ [SCN^{-}] = 2[S_{2}O_{3}^{2-}] + [S_{2}O_{3}^{2-}] + [S_{2}O_{3}^{2-}]. \]

The results obtained by the proposed method give serious errors with a recovery ranging from 80 to 90%. Mizoguchi and Okabe investigated the cyanolysis conditions and reported an improved method in which the amount of thiosulfate in the mixture was directly determined by procedure I. The cyanolysis of trithionate, which can not be ignored under the conditions of procedure II, is depressed to 0.7% by the addition of organic solvents such as acetone and methanol. When "[SCN^{-}] = [S_{4}O_{6}^{2-}]" is used, the amounts of the three sulfur species in their mixture are given by the following equations: 

\[ [S_{2}O_{3}^{2-}] = I, [S_{2}O_{3}^{2-}] = III-II \text{ and } [S_{2}O_{3}^{2-}] = (II-I)/2. \]

Here, I, II and III denote the molar concentrations of thiocyanate determined using the absorbance obtained by procedures I, II and III, respectively. This technique was applied to the determination of thiosulfate, trithionate and tetrathionate in flotation mill solutions. However, it is doubtful, as stated before, whether the cyanolysis of both tri- and tetrathionate proceeds to stoichiometric completion under the conditions in the procedure III. Because they were cyanolysed at a high temperature of boiling water for 30-45 min.

5-1-6 Tetrathionate-thiosulfate-sulfite-trithionate mixture

The proposed method for the determination of tetrathionate, thiosulfate, sulfite and trithionate in a mixture consists of four procedures; the excess iodine for thiosulfate and/or sulfite under procedures I, II and III, and the thiocyanate formed under procedure IV are measured spectrophotometrically after proper chemical treatments. These four sulfur compounds in their mixture give the following equivalents in the four procedures:

\[ [S_{2}O_{3}^{2-}] = [S_{4}O_{6}^{2-}] + [S_{2}O_{3}^{2-}], \]
\[ [S_{2}O_{3}^{2-}] = [S_{4}O_{6}^{2-}], \]
\[ [S_{2}O_{3}^{2-}] = [S_{4}O_{6}^{2-}] + 2[S^{2-}], \]

and

\[ [SCN^{-}] = 2[S_{2}O_{3}^{2-}] + [S_{2}O_{3}^{2-}] + [S_{2}O_{3}^{2-}]. \]

Under procedure I, the thiosulfate formed by sulfitolysis of tetrathionate reacts with iodine. Therefore, the absorbance obtained by procedure I corresponds to the sum of the amount of tetrathionate and that of thiosulfate in the mixture [see Eqs. (1) and (3), and Fig. (3)]. The absorbance obtained by procedure II, in which the sulfitolysis of tetrathionate was not carried out and the sulfite in the mixture was masked by formaldehyde, corresponds only to the amount of thiosulfate in the mixture. The absorbance obtained by procedure III, in which neither the sulfitolysis of tetrathionate nor the masking of sulfite was carried out, corresponds to the sum of the amount of thiosulfate and twice that of sulfite in the mixture. The absorbance obtained by procedure IV, in which tetrathionate was converted into both thiosulfate and trithionate according to Eq. (3), followed by their conversion into thiocyanate by the cyanolysis, corresponds to the sum of the amount of thiosulfate [Eq. (9)], that of trithionate [Eq. (12)] and twice that of tetrathionate [Eq. (20) and Fig. (4)] in the mixture. Hence, the following equations can be obtained for the four sulfur compounds in their mixture: 

\[ [S_{2}O_{3}^{2-}] = I-II, [S_{2}O_{3}^{2-}] = II, [S_{2}O_{3}^{2-}] = (III-II)/2 \text{ and } [S_{2}O_{3}^{2-}] = IV-2I+... \]
II. Here, I, II and III indicate the molar concentrations of thiosulfate determined using the absorbance obtained by procedures I, II and III, respectively, and IV denotes the molar concentrations of thiocyanate determined by procedure IV.

The thiosulfate and trithionate formed by the sulfitolysis of tetrathionate were quantitatively converted into thiocyanate over the pH ranges 9.3 - 9.6 and 8.9 - 9.6, respectively, when cyanolyzed for 1.5 h at 15°C. Consequently, both of the thiosulfate and trithionate formed from tetrathionate and those in the mixture were stoichiometrically converted into thiocyanate over the pH range 9.3 - 9.6. The following overall reaction for tetrathionate therefore can be obtained under the conditions in procedure IV:

\[
\text{S}_4\text{O}_6^{2-} + 4\text{CN}^- + \text{H}_2\text{O} \rightarrow \text{SO}_3^{2-} + \text{SO}_4^{2-} + 2\text{HCN} + 2\text{SCN}^-.
\] (20)

The calibration graph obtained for tetrathionate by measuring the thiocyanate formed from tetrathionate, shown in Fig. 4, coincided with that for thiocyanate when the molar concentration scale for tetrathionate is drawn to twice the scale for the thiocyanate concentration. Figure 4 confirms that tetrathionate was completely converted into thiocyanate according to Eq. (20) and further that the thiosulfate and trithionate in the mixture were converted into thiocyanate according to Eqs. (9) and (12), respectively.

Of course, the proposed method is applicable not only to a mixture of trithionate and tetrathionate, but also to a mixture of thiosulfate, trithionate and tetrathionate. \([\text{S}_3\text{O}_6^{2-}] = \text{IV} - 2\text{I} \) and \([\text{S}_4\text{O}_6^{2-}] = \text{I} \) can be obtained for the trithionate-tetrathionate mixture, and \([\text{S}_2\text{O}_3^{2-}] = \text{II} \), \([\text{S}_3\text{O}_6^{2-}] = \text{IV} - 2\text{I} + \text{II} \) and \([\text{S}_4\text{O}_6^{2-}] = \text{I} - \text{II} \) for the thiosulfate-trithionate-tetrathionate mixture. Analytical methods for mixtures of six to seven sulfur species, such as trithionate-tetrathionate-pentathionate-hexathionate-thiosulfate-sulfite-sulfide mixture, can be expected to be available provided that, in addition to sulfitolysis and cyanolysis of polythionates, sulfidolysis and other chemical reactions of the polythionates are used as additional procedures.

5-2 Electroanalytical methods

The polarographic behavior of tri-, tetra- and pentathionate has been investigated using potassium chloride, potassium iodide and hydrochloric acid in the base solutions. The half-wave potentials vs. SCE obtained are, respectively, \(-1.34 \text{ V} \) for trithionate in a medium of 1 M potassium chloride in 50% alcohol, \(-0.285 \text{ V} \) for tetrathionate in 1 M hydrochloric acid and \(-0.3 \text{ V} \) in 1 M potassium chloride-0.01% gelatin, and \(-0.211 \text{ V} \) for pentathionate in 2 M hydrochloric acid. The tetrathionate in a mixture of tri- and tetrathionates can be determined by using 1 M hydrochloric acid as the supporting electrolyte. The total amounts of tri- and tetrathionate are then determined by using a polarographic medium of 1 M potassium chloride-0.01% gelatin–50% alcohol; in this base solution the reduction waves of the two polythionates overlap. Pentathionate can be determined in the presence of tetrathionate only when polarographed in 2 M hydrochloric acid in 50% alcohol; the tetrathionate does not give any reduction process in this medium. Trithionate could not be determined in the presence of pentathionate since the polarogram of the latter shows a depression at about \(-1.15 \text{ V} \) vs. SCE in alcoholic potassium chloride solutions.

On the other hand, the mixture containing tetra-, penta- and hexathionate was analyzed by coupling thin-layer high-voltage electrophoresis with coulometric titration or ultraviolet spectrophotometry.

5-3 Chromatographic separations

5-3-1 Classical anion-exchange chromatography

Di-, tri-, tetra- and pentathionate in their mixture, as well as the constituents of Wackenroder’s solution, were separated by using Dowex 1-X2 in the chloride form of 50 to 100 mesh. Dithionate is first eluted with 1 M hydrochloric acid; at this stage any oxyanions of sulfur other than polythionates are eluted out before the dithionate. Then trithionate is eluted with 3 M HCl, tetrathionate with 6 M HCl, and finally pentathionate with 9 M HCl. Pollard et al. began the elution first with potassium hydrogen phthalate and then with hydrochloric acid, and achieved the separation of the polythionates up to pentathionate, thiosulfate and sulfite. In addition, mixtures of \(\text{S}_2\text{O}_3^{2-} - \text{SO}_3^{2-} - \text{S}_3\text{O}_6^{2-}\) and \(\text{S}_3\text{O}_6^{2-} - \text{S}_4\text{O}_6^{2-} - \text{S}_2\text{O}_3^{2-}\) could be separated without difficulty using sodium chloride or hydrochloric acid as eluents. However, the separation of hexathionate was not possible due to its decomposition on the column.

5-3-2 Modern liquid chromatography

A number of publications dealing with the liquid chromatography of polythionates have appeared and...
quite different chromatographic conditions have been used for the separation of the polythionates. Chapman and Beard\textsuperscript{70} used an activated carbon column with ultraviolet absorption detection at 254 nm for the separation and determination of polythionates and thiosulfate in Wackenroder's solution. However, difficulty in preparing reproducible columns of activated carbon has been encountered and the sensitivity for trithionate is quite low, leading at times to problem with detection. Wolkoff and Larose\textsuperscript{71} suggested a method using a commercially available anion-exchange column and applied it to the determination of the polythionates and thiosulfate in mining wastewaters and environmental samples. The detection system employed herein involves reaction of the polythionates in the column effluent with base and then oxidation of both the thiosulfate and sulfite formed with cerium(IV) with subsequent fluorometric detection of cerium(III). The relative molar responses obtained for polythionates were not close to the theoretical values probably because the alkaline decomposition of the polythionates did not go to stoichiometric completion. Story\textsuperscript{72} also employed anion-exchange liquid chromatography to separate polythionates. His technique requires a postcolumn reaction for the polythionates to be detectable; the polythionate anions in the column effluent are oxidized with bromine and the resulting sulfate is measured as FeSO$_4^{+}$ after addition of iron(III) to the effluent stream. Takano et al.\textsuperscript{73} used a differential pulse polarographic technique to determine the polythionates and thiosulfate in the anion-exchange column effluent. However, they failed to separate tri- and tetrathionate chromatographically. A sample aliquot was therefore sulfitolyzed\textsuperscript{45} prior to a high performance liquid chromatographic (HPLC) separation, followed by a subsequent polarographic measurement of the resulting thiosulfate and trithionate. On the other hand, retention times in anion-exchange liquid chromatography for polythionates (S$_x$O$_{6-2x}$: $x=3$, 4, 5 and 6) could be fairly readily predicted using a plot of log retention time vs. $x$, which gives a straight line.\textsuperscript{74}

Though reversed-phase ion-pair chromatography has proven to be a valuable technique for the separation of organic solute, this technique had not been widely utilized for inorganic ions. This can be attributed to the poor detectability of most inorganic ions by the 254-nm ultraviolet detector prevalent in HPLC systems. Ion-pair chromatography\textsuperscript{75} on a Hamilton Resin PRP-1 reversed phase column with conductivity detection made possible the separation of polythionates in mixtures with thiosulfate. Optimization conditions include the use of tetrapropylammonium bromide (TPABr) as an ion-pair reagent. Retention was dependent on the nature of both the cation and the anion of the ion-pair reagent. Results of a typical chromatogram of a mixture of thiosulfate, tri-, tetra- and pentathionate are presented in Table 2. A convenient alternative has been offered by using UV-absorbing quaternary ammonium ion-pair reagents. Steudel and Holdt\textsuperscript{76} separated polythionates in their mixture by ion-pair chromatography on a Dionex MPIC-NS1 column with 254-nm UV detection using an eluent containing 27% acetonitrile, 4% methanol, 69% water, 0.001 M sodium carbonate and 0.002 M tetrabutylammonium hydroxide. The chromatographic separation of thiosulfate and the polythionates with up to six sulfur atoms is shown in Fig. 5. In addition, they prepared a mixture containing other higher polythionate anions ($x>6$) by treating a mixture of dichlorosulfanes S$_x$Cl$_2$ ($x=1$–7) with thiosulfate according to the following equation:

\[ 2\text{Na}_2\text{S}_2\text{O}_3 + \text{S}_x\text{Cl}_2 + 2\text{HCl} \rightarrow \text{H}_2\text{S}_4\text{O}_6 + 4\text{NaCl}. \] (21)

The peak identification in the chromatograms obtained for the above polythionate mixtures, however, causes problems since pure or almost pure polythionates higher than hexathionate are not available.

References
