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The Rapid Determination of Sulfide, Thiosulfate, and Polysulfide in the Lixiviation Water of Blast-furnace Slag by Means of Argentimetric Potentiometric Titration

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Sulfide, thiosulfate, and polysulfide ions in their mixtures were determined potentiometrically with a silver-nitrate standard solution. These three species can be precisely determined from two titrations for each sample with the coefficient of variation of 0.3% at the concentration level of 5×10^{-4} M (1 M=1 mol dm^{-3}). One aliquot is titrated, after making the titrand acidic with an acetate buffer (pH=4), to get the end points of the sulfide and thiosulfate ions respectively, in the presence of free sulfur. The other is titrated, after the sulfitolysis of the sample solution, to show the end points of the sulfide and thiosulfate(the original thiosulfate plus the thiosulfate which is formed from polysulfide) ions in the presence of excess sulfite. The addition of calcium nitrate is effective in making the end points clear and accurate. This method was applied to determine these species in lixiviation water of blast-furnace slag.

Elemental sulfur dissolves in an alkaline solution of sulfide to form polysulfides:[1)]

$$x\mathrm{S} + \mathrm{S}^{2-} \longrightarrow \mathrm{S}_{x+1}^{2-}. \qquad (1)$$

In addition, sulfur[2)] reacts with alkali hydroxide to produce sulfide, polysulfide, and thiosulfate through the following equation:

$$(4+2x)\mathrm{S} + 6\mathrm{OH}^- \longrightarrow 2\mathrm{S}_{x+1}^{2-} + \mathrm{S_2O_3}^{2-} + 3\mathrm{H_2O}. \qquad (2)$$

Therefore, there are many cases which involve these three species together, *e.g.*, sulfide, thiosulfate, and polysulfide, in such solutions as the lixiviation water of blast-furnace slag.[3),13)]

One sulfur atom in each polysulfide ion is denoted as sulfide sulfur(S^{2-}), while the rest of the ion(S_x) is denoted as polysulfide sulfur (or dissolved sulfur).[11)]

Various methods, such as potentiometric,[4),5)] biamperometric,[6)] and iodometric methods,[2)] to determine S^{2-}, $\mathrm{S_2O_3}^{2-}$, and S_x in a polysulfide solution have already been presented. Blasius and his co-workers[3),14)] determined sulfur compounds in the lixiviation water of blast-furnace slag by photometric and titrimetric methods. Most of these methods are, however, rather complicated and time-consuming because of the necessity of separation, masking, and several titrations. Papp and Havas[7)] determined these three species potentiometrically by using a sulfide-ion-selective electrode as the indicator; they added an excess amount of sulfite to the sample solution, and the resultant $\mathrm{S_2O_3}^{2-}$, equivalent to the S_x, was titrated with a mercury(II) chloride solution. Although this method is simple and useful, there are some problems, such as water pollution due to waste mercury and the necessity of masking the excess sulfite ions with formaldehyde. It was previously reported[8),9)] that $\mathrm{S_2O_3}^{2-}$ in the presence of large amounts of $\mathrm{SO_3}^{2-}$ could be titrated with the silver ion by utilizing the formation of thiosulfatoargentate or silver sulfide in an acidic solution without masking $\mathrm{SO_3}^{2-}$ with formaldehyde. Sulfide, $\mathrm{S_2O_3}^{2-}$, and $\mathrm{SO_3}^{2-}$ could also be determined[10)] directly by the three successive argentimetric titrations of the same sample solution in the presence of calcium nitrate. Sulfide and S_x in a polysulfide solution could be determined[11)] after the cyanolysis of the polysulfide, but the end points were affected by the presence of $\mathrm{S_2O_3}^{2-}$. In these investigations, silver–silver sulfide, silver–silver iodide, and silver-ion-selective electrodes were used.

The present paper reports a method of determining S^{2-}, S_x, and $\mathrm{S_2O_3}^{2-}$ in a synthetic polysulfide solution and the lixiviation water of blast-furnace slag by argentimetric potentiometric titration with silver–silver sulfide, silver–silver iodide, and saturated-calomel electrodes. The advantage of this method is that the contents of these three species can be determined from two titrations for each sample. One aliquot is titrated, after making the titrand acidic with an acetate buffer (pH=4), to give the end points of S^{2-} and $\mathrm{S_2O_3}^{2-}$ in the presence of elemental sulfur. The other is titrated, after the sulfitolysis of the sample solution, to give the end point of S^{2-} and that of $\mathrm{S_2O_3}^{2-}$ plus S_x in the presence of sulfite:

$$\mathrm{S}_{x+1}^{2-} \xrightarrow{\mathrm{H}^+} \mathrm{HS}^- + \mathrm{S}_x, \qquad (3)$$

$$\mathrm{S}_{x+1}^{2-} + x\mathrm{SO_3}^{2-} \longrightarrow \mathrm{S}^{2-} + x\mathrm{S_2O_3}^{2-}, \qquad (4)$$

$$\mathrm{S_2O_3}^{2-} + \mathrm{Ag}^+ \longrightarrow \mathrm{Ag(S_2O_3)}^-. \qquad (5)$$

Experimental

Reagent and Apparatus. All the chemicals used were of a reagent grade. Oxygen-free redistilled water was used for the preparation of all solutions. The stock solution of polysulfide was prepared and stored by a method described previously.[11)] Working solutions were prepared by the further dilution of the stock solution.

An automatic recording potentiometric titrator, Hiranuma RAT-101, with a silver–silver sulfide or a silver–silver iodide electrode, together with a saturated calomel electrode, was used.

Procedure. *Assay of* S^{2-} *and* $\mathrm{S_2O_3}^{2-}$ *in* S_{x+1}^{2-}: Place a definite amount of a sample solution in a titration cell containing 10 ml of oxygen-free water and a 1-cm-thick liquid-paraffin layer. Add, successively, 2 ml of 1 M calcium nitrate, acetic acid, or acetate buffer to adjust the pH to 4 and oxygen-free water to make the volume up to about 100 ml, which should then be gently poured against the wall of the cell so that air bubbles are not entrained. Titrate this solution potentiometrically with 0.1 M silver nitrate solution using a silver–silver sulfide indicator electrode until the titration curve shows a sudden change, which corresponds to the end point for S^{2-} (Fig. 1, 1-A). Then replace the

Table 1. Determination of sulfide and thiosulfate in polysulfide solutions

$[S^{2-}]$/M	$[S^0]$/mg	$[S_2O_3^{2-}]$/M	Difference/% S^{2-} b)	Difference/% $S_2O_3^{2-}$ c)	Coefficient of variation/% S^{2-}	Coefficient of variation/% $S_2O_3^{2-}$
5×10^{-4}	0.5	5×10^{-4}	+0.3	−0.5	0.3	0.3
5×10^{-4}	1.6	5×10^{-4}	−0.3	±0.0	0.3	0.3
5×10^{-4}	3.2	5×10^{-4}	+0.3	+0.9	0.1	0.3
5×10^{-4}	5.0	2.5×10^{-4}	+0.2	±0.0	0.1	0.5
5×10^{-5}	0.16	5×10^{-5}	+1.1	+1.9	0.3	0.7
5×10^{-4}	1.6	10^{-4}	−0.4	+0.3	0.2	0.2
5×10^{-4}	1.6	2.5×10^{-4}	−0.2	+0.7	0.1	0.5
5×10^{-4}	1.6	10^{-5} a)	+0.5	+5.8	0.1	3.7

Titrant: 0.1 M $AgNO_3$. Each value is the average of 4 titrations. a) Standard addition method. b) Compared with the mercury(II) chloride method.[7] c) Compared with the iodometric method.[2]

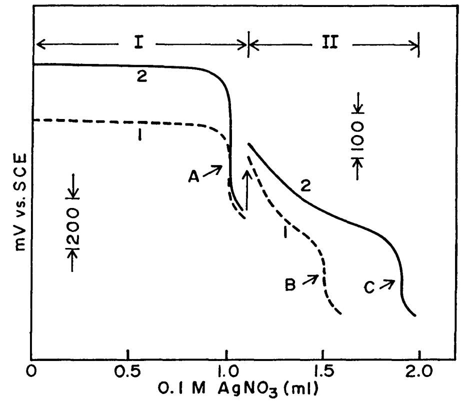

Fig. 1. Potentiometric titration curves for sulfide, polysulfide–sulfur, and thiosulfate in polysulfide solution.
Sample solution: 100 ml of 5×10^{-4} M Na_2S_{x+1} (S^0= 1.6 mg) and 5×10^{-4} M $Na_2S_2O_3$.
1: Without sulfitolysis. Titration medium: 10^{-2} M $Ca(NO_3)_2$ and 2×10^{-2} M acetate buffer (pH=4).
2: With sulfitolysis. Titration medium: 10^{-2} M $Ca(NO_3)_2$ and 0.1 M NH_3 up to the end point related to S^{2-}, then pH 1.5—3 (with 0.5 M H_2SO_4).
I: Ag–Ag_2S electrode, II: Ag–AgI electrode. A: S^{2-}, B: $S_2O_3^{2-}$, C: S^0.

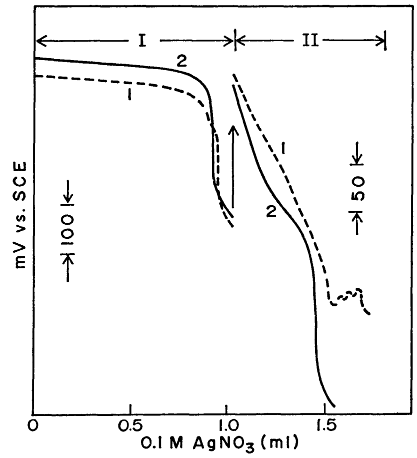

Fig. 2. Effect of calcium ion on the titration curves for sulfide and thiosulfate in polysulfide solution. Sample solution: 100 ml of 5×10^{-4} M Na_2S_{x+1} (S^0= 1.6 mg), 5×10^{-4} M $Na_2S_2O_3$ and 2×10^{-2} M acetate buffer (pH=4).
1: Without $Ca(NO_3)_2$, 2: With 10^{-2} M $Ca(NO_3)_2$
I: Ag–Ag_2S electrode, II: Ag–AgI electrode.

indicator electrode by a silver–silver iodide and continue the titration until the end point for $S_2O_3^{2-}$ (Fig. 1, 1-B) is reached.

Assay of S^{2-} and S_x in S_{x+1}^{2-}: Add 10 ml of 0.5 M sodium sulfite and 30 ml of oxygen-free water to a sample solution which has been prepared in the manner described above. Heat this to about 50 °C and then allow it to stand for 3 min. Cool the solution below 15 °C. Add 10 ml of 1 M ammonia and 2 ml of 1 M calcium nitrate, and bring the total volume to about 100 ml with oxygen-free water. Titrate this solution with 0.1 M silver nitrate by using a silver–silver sulfide indicator electrode until the titration curve shows a sudden change for S^{2-} (Fig. 1, 2-A). Then adjust the pH to 1.5—3 with 0.5 M sulfuric acid and continue the titration until the end point for $S_2O_3^{2-}$ plus S_x is reached (Fig. 1, 2-C) by using a silver–silver iodide indicator electrode.

The S^{2-} (free sulfide plus the sulfide bound by polysulfide) content is obtained by the use of the end point(A). The original $S_2O_3^{2-}$ content is calculated from the difference between (A) and (B). The S_x content (measured as $S_2O_3^{2-}$) is estimated by (C) minus (B).

Results and Discussion

Determination of Sulfide, Thiosulfate, and Polysulfide–Sulfur in a Synthetic Polysulfide Solution. Figure 1 shows some typical titration curves. Acetate buffer (pH=4) and calcium nitrate were added in order to isolate elemental sulfur and to get clear and accurate end points for S^{2-} and $S_2O_3^{2-}$. Calcium nitrate may be considered to have a coagulating action to the elemental sulfur isolated from the S_{x+1}^{2-} and silver sulfide produced during the titration. Figure 2 shows the effect of calcium nitrate on the titration of sulfide and thiosulfate ions in a polysulfide solution. The end point of $S_2O_3^{2-}$ was obtained by the formation of thiosulfatoargentate. The solution was protected from the evolution of hydrogen sulfide by covering it with a liquid-paraffin layer. Table 1 shows the results thus obtained from solutions with various concentrations. The S^{2-} and $S_2O_3^{2-}$ contents ranging from 10^{-4} to 5×10^{-4} M in the polysulfide solution could be determined with a good accuracy and reproducibility.

On the other hand, the S_x in polysulfide solution

Table 2. Determination of sulfide, thiosulfate, and polysulfide-sulfur

$[S^{2-}]$/M	$[S^0]$/mg	$[S_2O_3^{2-}]$/M	Difference/%			Coefficient of variation/%		
			S^{2-} b,c)	S^0 c)	$S_2O_3^{2-}$ d)	S^{2-}	S^0	$S_2O_3^{2-}$
5×10^{-4}	0.5	5×10^{-4}	+1.1	+0.5	−0.5	0.1	0.5	0.3
5×10^{-4}	1.6	5×10^{-4}	+0.5	+0.2	±0.0	0.1	0.3	0.3
5×10^{-4}	3.2	5×10^{-4}	+0.3	−0.2	+0.9	0.1	0.3	0.3
5×10^{-4}	5.0	2.5×10^{-4}	+1.3	−2.6	±0.0	0.3	0.2	0.5
5×10^{-5}	0.16	5×10^{-5}	−1.1	+4.3	+1.9	0.6	0.5	0.7
5×10^{-4}	1.6	10^{-4}	+0.8	−1.3	+0.3	0.2	0.3	0.2
5×10^{-4}	1.6	2.5×10^{-4}	+0.1	+0.4	+0.7	0.2	0.4	0.5
5×10^{-4}	1.6	10^{-5} a)	+0.6	−1.1	+5.8	0.2	0.2	3.7

Titrant: 0.1 M $AgNO_3$. Each value is the average 4 titrations. a) Standard addition method. b) The result determined after sulfitolysis. c) Compared with the mercury(II) chloride method.[7] d) Compared with the iodometric method.[2]

Table 3. Determination of sulfide, thiosulfate, and polysulfide-sulfur in lixiviation water of blast-furnace slag

Sample	S^{2-} (mM)				S^0 (mM)				$S_2O_3^{2-}$ (mM)			
	I		II		I		II		I		II	
	Found a)	C.V. b)	Found a)	C.V. b)	Found a)	C.V. b)	Found a)	C.V. b)	Found a)	C.V. b)	Found a)	C.V. b)
A	2.00	0.2	1.99	0.4	3.91	0.7	3.92	0.6	8.09	0.4	8.07	0.3
B	1.35	0.5	1.30	0.6	3.36	0.9	3.44	0.5	8.27	0.3	8.27	0.3
C	2.93	0.5	2.87	0.4	3.06	0.7	3.14	0.5	8.10	0.3	8.32	0.4

I: Iodometric method[2,12]. II: Proposed method. a) Average of 4 titrations. b) Coefficient of variation. A sample solution was prepared by immersing 450 g of blast-furnace slag in 450 ml of demineralized water for 4 d.

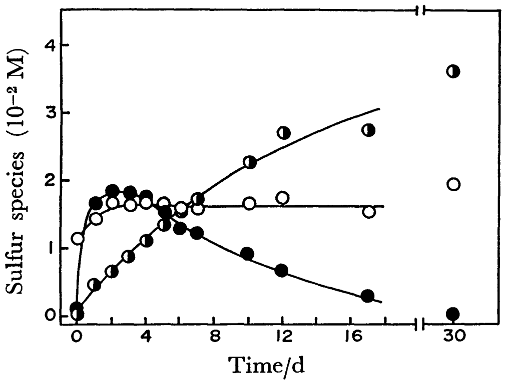

Fig. 3. Variation of sulfide, thiosulfate and polysulfide-sulfur in lixiviation water with the lapse of time. Sample: Slag(700 g)+Demineralized water(300 ml). Sample was placed in a dark room at 30 °C. —◐—: S^{2-}, —○—: $S_2O_3^{2-}$, —●—: $S_x^{2-}(S^0)$.

was determined after converting it to $S_2O_3^{2-}$ through a reaction with SO_3^{2-}. An excess amount of SO_3^{2-} had no effect on the determination. The resulting solution was first titrated, after the addition of ammonia and calcium nitrate, to get the end point of S^{2-}, and then, after adjusting the titrand pH to 1.5—3, the titration was continued until the end point of $S_2O_3^{2-}$ (the original $S_2O_3^{2-}$ plus the $S_2O_3^{2-}$ produced from S_x) was attained. Any mixture containing each of the three species in various concentrations could be determined by the proposed method with a good accuracy and reproducibility, as is shown in Table 2. The analytical values for S_x in S_{x+1}^{2-} were identical to those determined by the mercury(II)–chloride method.[7]

The presence of sodium hydroxide, sodium carbonate, and sodium sulfate(the concentration of each being 2.5×10^{-2} M) did not disturb the determination.

Determination of Sulfide, Thiosulfate, and Polysulfide–Sulfur in Lixiviation Water of Blast-furnace Slag. The lixiviation waters were prepared by immersing 450-g portions of three different examples of blast-furnace slag (A, B, and C) in 450 ml of demineralized water for 4 d. Each lixiviation water was covered with a liquid-paraffin layer to prevent air oxidation. The contents of S^{2-}, $S_2O_3^{2-}$, and S_x in the lixiviation waters were then determined by the proposed method, and the values were compared with those obtained with other methods.[2,12] The results are shown in Table 3. When a 700-g portion of blast-furnace slag was immersed in 300 ml of water, the concentration variations of S^{2-}, $S_2O_3^{2-}$, and S_x in the lixiviation water with the lapse of time were as is shown in Fig. 3.

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