Coagulated Ion-exchanger Colorimetry for the Determination of Trace Amounts of Sulfide as Methylene Blue

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Synopsis. Sulfide ion was converted to Methylene Blue through the reaction with *N,N*-dimethyl-*p*-phenylenediamine in the presence of iron(III) ion. The dye produced was fixed by batch method onto the coagulated mixture of finely divided anion and cation exchange resins. The coagulated material was collected by filtration on a filter paper as a disk of thin layer, which was then soaked in an acetate buffer solution, and subjected to the spectrophotometric analysis. The calibration graph was linear over the range 1.03—10.3 nmol of sulfide. The method was applied to some hot spring waters.

The most familiar method for the determination of sulfide is the Methylene Blue method,[1,2] which was recommended by Emil Fisher as early as 1883.[3] The sensitivity of the method is rather high but the enrichment is usually required for the determination of trace amounts of sulfide in water. Recently, a flotation method was reported,[4] in which the Methylene Blue formed through the reaction of sulfide with *N,N*-dimethyl-*p*-phenylenediamine in the presence of iron(III) ion was separated by flotation with sodium dodecyl sulfate. Down to 2 μg of sulfide in 1-dm³ sample solution was determined.

In the present paper, the coagulated ion-exchanger colorimetry[5,6] is examined for the Methylene Blue method. The colored compound is concentrated in the thin layer of mixed ion exchange resins by a factor greater than 700 and determined spectrophotometrically.

Experimental

Reagents. A 0.1 w/v% solution of *N,N*-dimethyl-*p*-phenylenediammonium sulfate (abbreviated as DPDA, Wako Pure Chemicals) was prepared by dissolving 0.1 g of the reagent in 100 ml of 5 mol dm^{-3} sulfuric acid. A 0.1 mol dm^{-3} iron(III) chloride solution was prepared by dissolving 2.7 g of iron(III) chloride hexahydrate in 50 ml of hydrochloric acid and then diluting to 100 ml with water. An aqueous 1.0% zinc(II) acetate solution was prepared. The crystals of sodium sulfide nonahydrate, $Na_2S \cdot 9H_2O$, were rinsed with a small amount of water and dried and stored under nitrogen atmosphere. A 0.01 mol dm^{-3} sulfide solution was prepared by dissolving dried reagent in oxygen-free water and standardized immediately before use by iodometry. The sulfide standard solution was prepared fresh every time when the determination was carried out. The solution was diluted 100 times with oxygen-free water and further 100 times with the zinc(II) acetate solution to give a 1.0 μmol dm^{-3} solution. Methylene Blue used was a Merck product for microscopy. The reagent was dried for 4 h at 105 °C, and aqueous 1.0 mmol dm^{-3} stock solution was prepared.

Ion Exchange Resin Suspension. The macroreticular type ion exchangers, Amberlyst 15 and A-27 (Rohm and Haas), were used in RSO_3H and $RN(CH_3)_3Cl$ forms, respectively. The cation exchange resin suspension (CRS) and anion exchange resin suspension (ARS) were prepared according to the method reported.[7] The exchange capacities were 11.8 μequiv ml^{-1} for CRS and 7.0 μequiv ml^{-1} for ARS. When a 2.0-ml portion of CRS was mixed with 4.0 ml of ARS, both resins were coagulated completely with each other and the mixed resins were easily and quantitatively collected on a filter paper.

Apparatus. A Shimadzu UV 140-01 spectrophotometer was used. A Toyo KG-25 filter holder was used with filter papers of No. 5B (Toyo Roshi). A vaccum guage used was a NRK product, type STV-75.

General Procedure. A 25-ml portion of the zinc(II) acetate solution was placed in a 100-ml separatory funnel, and a sample solution containing less than 10.3 nmol of sulfide was added, and then the solution was diluted to 50 ml with the zinc(II) acetate solution. A 5-ml portion of DPDA solution and 1 ml of the iron(III) chloride solution were quickly added and the reaction mixture was shaken vigorously for 1 min and allowed to stand for 60 min. A 4.0-ml portion of ARS and 2.0 ml of CRS were then added to the solution and the mixture was shaken for 10 min. The resulting coagulated resins were collected on the filter strip placed on the holder by filtration with suction (600 mmHg). A disk of colored thin layer, 17 mm in diameter and about 0.3 mm in thickness, was formed. The filter strip supporting the thin layer was soaked in the acetate buffer solution (pH 4.6) for 15 min, and it was fixed on a glass plate on the one side of cell holder which is nearer to the light source. The absorbance was measured at 675 nm against the dry filter paper or another white paper. Another disk of thin layer was prepared without addition of sulfide and the absorbance corresponding to the reagent blank including the resins was also measured. The net absorbance of Methylene Blue in the resin phase was determined by substruction. Fundamental experiments were performed according to the above procedure with the exception that the pure Methylene Blue solution was used instead of the standard sulfide solution.

Results and Discussion

Adsorption of Methylene Blue. Methylene Blue was found to be strongly fixed on the cation exchange resin. The cation exchange resin was coagulated with anion exchange resin to form a bulky material and separated from the bulk solution within 8 min. The disk of colored thin layer with a smooth surface was obtained on the filter paper. The volume of resin phase being about 0.07 cm³, Methylene Blue was concentrated from 50 ml of the reaction mixture by a factor greater than 700.

Adsorption Spectrum. The absorption spectrum of Methylene Blue in the resin phase was slightly shifted to longer wavelength compared with that in solution (Fig. 1). The effect of pH was studied. The pH of initial solution, from which Methylene Blue was fixed on the mixed resins, was kept at 0.8, and the resulting thin layer was soaked for 15 min in the solutions with various

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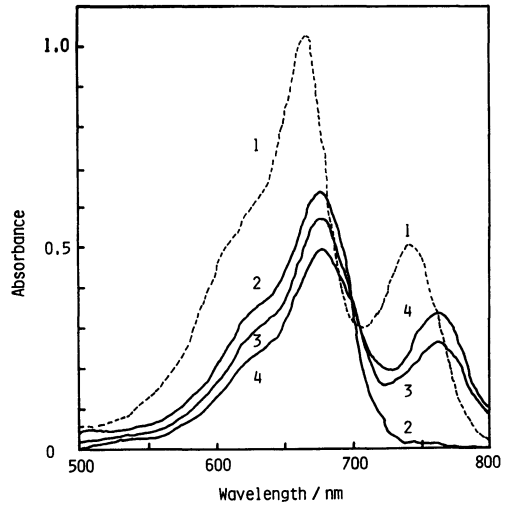

Fig. 1. Effect of pH on the absorption spectra of 6 nmol of Methylene Blue on the thin layer of mixed resins. The absorbance was measured after soaking the thin layer for 15 min in varying pH solutions; 2) 4.62, 3) 1.04, 4) 0.80. Dotted line (1) indicates the absorption spectrum of 20 μmol dm^{-3} Methylene Blue solution at pH 0.80 in a 1-cm cell.

Table 1. Effect of foreign ions on the determination of 6.25 nmol of sulfide ion

Compound	Added amount μmol	Absorbance at 675 nm	Error %
None	—	0.327	—
$NaNO_2$	0.06	0.320	−2.1
	0.60	0.319	−2.4
	6.00	0.196	−41.9
$NaHSO_3$	6.00	0.325	−0.6
$HSCH_2COONa$	6.56	0.354	+8.2

Table 2. Determination of sulfide in hot spring water

Sampling place	Sample amounts ml	Absorbance at 675 nm	Sulfide found ng S ml^{-1}
Shirogane	4.0	0.244	35.6
(pH = 6.76)	6.0	0.362	35.2
	6.0	0.364	35.4
	8.0	0.458	33.4
	8.0	0.496	36.2
			35.2±1.3[a)]
Nakagoya	0.5	0.488	569.5
(pH=9.11)	0.5	0.468	546.1
	0.5	0.476	555.5
			557.0±29.3[a)]

a) 95% confidence limits.

pH values. With increasing pH, the absorbance at the maximum of 675 nm increased, while that of 760 nm decreased, which indicates that the latter absorption maximum is due to the protonated Methylene Blue.[1)]

Effect of Soaking Time. When the thin layer was soaked in the acetate buffer solution of pH 4.6, the absorbance of Methylene Blue at 675 nm increased gradually and reached a constant value within 10 min. Thereafter the coloration was stable for at least 60 min. The use of acetate buffer soaking solution is advantageous for the sensitivity and stability of the coloration.

Standing Time of Reaction Mixture. When the color developing reagents were added to the test solutions with and without sulfide, a violet color appeared immediately in both solutions. The blank coloration faded gradually and after 60 min, the lower blank value and the stable coloration of Methylene Blue were obtained.

Calibration Graph. The calibration graph showed a good proportionality over range 1.03—10.3 nmol of sulfide, with absorbance ranging from 0.054 to 0.543. The relative standard deviations were 8.5% (n=4) for 1.03 nmol and 1.5% (n=5) for 10.3 nmol of sulfide. The yield of Methylene Blue from sulfide was estimated by comparing the slope of calibration curve with that of pure Methylene Blue. The reaction yield was calculated to 52.5%, while the value reported by Gustafsson was 66.7%.[1)]

Effect of Foreign Ions. As summarized in Table 1, a large amount of nitrite gave a serious negative error, which is due to the reduction of iron(III) ion.[4)] Mercaptoacetate gave a positive error.[8)]

Determination of Sulfide in Hot Spring Water. The sample waters were clear enough and so directly subjected to the analysis. The sulfide was precisely determined in the varying sample aliquots (Table 2). The pH of sample water at Nakagoya was higher than that at Shirogane, and the former contained sulfide in higher concentration than the latter.

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