An Improved Photometric Method for the Determination of Sulfite with Pararosaniline and Formaldehyde

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Many investigations have been made on the determination of sulfur dioxide based on the reaction of rosaniline and/or *p*-rosaniline with formaldehyde.[1-10] West and Gaeke[4] developed a method which involved the process of absorbing sulfur dioxide into a solution of sodium tetrachloromercurate, followed by the addition of the *p*-rosaniline hydrochloride and the formaldehyde to form a purple-colored sulfonic acid derivative of *p*-rosaniline. Present authors tried to apply the method to the analysis of sulfur in igneous rocks. The reproducible results, however, were not obtained

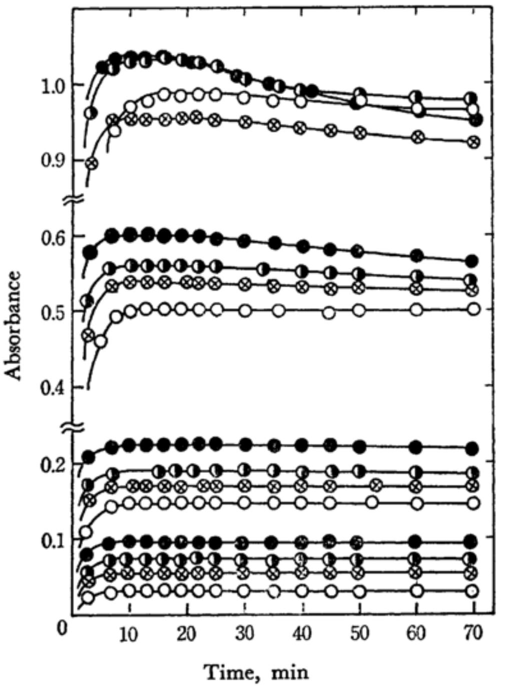

Fig. 1. Effects of temperature and concentration of sulfite on color development. Sulfite was dissolved in redistilled water.

—●— 40.0, 21.5, 5.4 μg of sulfur and reagent blank at 30°C.
—◑— 41.3, 20.9, 5.0 μg of sulfur and reagent blank at 25°C.
—⊗— 38.7, 20.9, 5.0 μg of sulfur and reagent blank at 20°C.
—○— 41.4, 20.7, 5.3 μg of sulfur and reagent blank at 10°C.

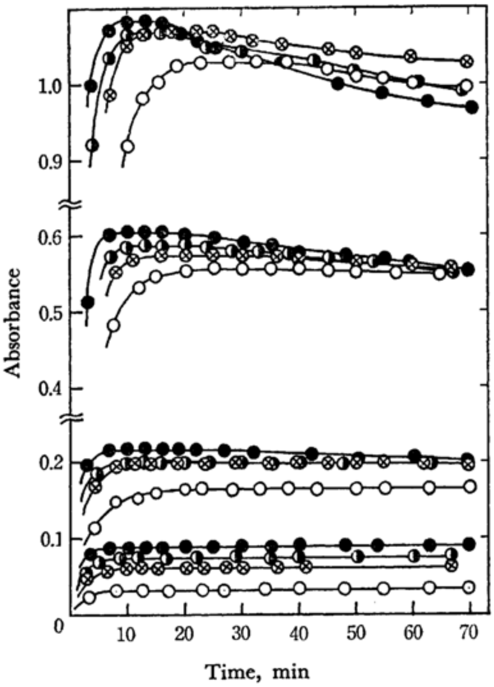

Fig. 2. Effects of temperature and concentration of sulfite on color development. Sulfite was dissolved in a 0.1 M sodium tetrachloromercurate solution.

—●— 40.5, 19.8, 4.7 μg of sulfur and reagent blank at 30°C.
—◑— 40.5, 19.7, 4.8 μg of sulfur and reagent blank at 25°C.
—⊗— 41.5, 19.8, 5.3 μg of sulfur and reagent blank at 20°C.
—○— 41.0, 20.5, 5.1 μg of sulfur and reagent blank at 10°C.

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under such experimental conditions,[4,7,8,10] because the color development depended on both the temperature and concentration of sulfite. Previous studies[3,4,7,10] on the effect of temperature on the color development were not satisfactory to the determination of sulfite at the various concentrations and temperatures.

Preparation of 0.04% *p*-Rosaniline Hydrochlolic Acid Solution. Exactly weighed 0.2 g of *p*-rosaniline hydrochloride was added in a small volume of redistilled water containing 15 ml of concentrated hydrochloric acid and then mixed well. After *p*-rosaniline dissolved completely, 15 ml of concentrated hydrochloric acid was added into the mixture, which was diluted exactly to 500 ml with the redistilled water. The color of this solution faded gradually from red to pale yellow. Reagent prepared by this method always showed constant absorbance and was stable for at least three months and also stable against light. No significant difference was observed in experimental results with the use of three *p*-rosaniline reagents from different sources.

Effects of Temperature and Concentration of Sulfite on Color Development. The effect of temperature on color development was examined for the solutions containing about 0, 5, 20 and 40 μg of sulfur as sulfite in 50 ml, respectively. A series of temperatures was chosen : 10, 20, 25 and 30°C. All the reagents and the redistilled water freshly boiled and cooled were kept in a thermostat adjusted at a desired temperature. Five milliliters each of the 0.04% *p*-rosaniline hydrochloric acid solution and the 0.2% formaldehyde solution were added to the sodium sulfite standard solution in the 50 ml volumetric flask. Then the contents were mixed well and diluted to the mark with the redistilled water or a 0.1 M sodium tetrachloromercurate solution. Flasks were kept in the thermostat. The absorbance of the colored solution was measured every several minutes at the wavelength of 562 mμ using the redistilled water as a reference. Results for sulfite in the redistilled water and for sulfite in the 0.1 M sodium tetrachloromercurate solution were shown in Figs. 1 and 2, respectively. As can be seen in Figs. 1 and 2, each colored solution had a time range in which the absorbance remained maximum. The length of these ranges depended on both the temperature and the concentration of sulfite. In order to obtain the reproducible results, the measurement of

TABLE 1. TIME RANGES OF CONSTANT ABSORBANCE

Temperature °C	Time range (min)	
	A	B
10	14—34	21—40
20	8—25	14—25
25	8—22	9—17
30	7—15	8—15

A: Sulfite was dissolved in redistilled water.
B: Sulfite was dissolved in a 0.1 M sodium tetrachloromercurate solution.

TABLE 2. EFFECTS OF DIVERSE IONS

Ion	Added as	Concn. mg/50 ml	Absorbance	
			Reagent blank	SO_3^{2-} 20 μg(as sulfur)
None		0	0.056±0.001	0.516±0.008
Na^+	$NaNO_3$	50	0.053	0.510
Ca^{2+}	$Ca(NO_3)_2 \cdot 4H_2O$	50	0.048	0.504
Mg^{2+}	$Mg(NO_3)_2 \cdot 6H_2O$	50	0.047	0.487
Al^{3+}	$Al(NO_3)_3 \cdot 9H_2O$	5	0.056	0.522
Fe^{3+}	$Fe(NO_3)_3 \cdot 9H_2O$	5	0.058	0.060
Fe^{2+}	$FeSO_4 \cdot 7H_2O$	5	0.055	0.456
F^-	NaF	5	0.061	0.515
Cl^-	NaCl	250	0.044	0.484
		5	0.056	0.513
Br^-	KBr	5	0.056	0.517
I^-	KI	5	0.056	0.509
SO_4^{2-}	Na_2SO_4	250	0.064	0.519
$S_2O_3^{2-}$	$Na_2S_2O_3 \cdot 5H_2O$	5	>1.200	>1.200
$S_4O_6^{2-}$	$K_2S_4O_6$	0.5	0.061	0.521
$S_5O_6^{2-}$	$K_2S_5O_6 \cdot 1.5H_2O$	0.5	0.059	0.512
$S_6O_6^{2-}$	$K_2S_6O_6$	0.5	0.059	0.512
S^{2-}	$Na_2S \cdot 9H_2O$	5	0.795	0.860
NO_2^-	$NaNO_2$	5	0	0
NO_3^-	KNO_3	50	0.055	0.512
PO_4^{3-}	NaH_2PO_4	5	0.059	0.512
AsO_4^{3-}	$Na_2HAsO_4 \cdot 7H_2O$	5	0.057	0.513

absorbance must be made within these time ranges of constant absorbance. The optimum ranges for the determination of sulfite up to the concentration of 40 μg of sulfur were decided referring to Figs. 1 and 2. These were shown in Table 1.

Calibration Curves. Using sodium sulfite standard solution, calibration curves were obtained by measuring the absorbance within the time ranges shown in Table 1 at each temperature. The calibration curve for sulfite in the redistilled water was straight and that for sulfite in the 0.1 M sodium tetrachloromercurate solution was somewhat curved. In both cases the calibration curves at each temperature were parallel with each other.

Effects of Diverse Ions. To examine the effects of diverse ions on this method, some experiments were made in the presence of 20 μg of sulfite sulfur and its absence at 20°C. The results were shown in Table 2.