

A NEW SPECTROPHOTOMETRIC REAGENT FOR DETERMINATION OF SULPHUR DIOXIDE AND FORMALDEHYDE

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ABSTRACT

Auramine was used for spectrophotometric determination of sulphur dioxide and formaldehyde in trace amounts. λ_{max} for sulphur dioxide and formaldehyde determination were at 366 and 362 nm respectively against the reagent blanks. The Beer's law and Sandell sensitivity values for sulphur dioxide determination ranged from 0.08–8.12 ppm and $0.008 \mu\text{g cm}^{-2}$ respectively; the values for formaldehyde determination were respectively 0.02–2.60 ppm and $0.002 \mu\text{g cm}^{-2}$. The tolerance limits of various foreign species in the determination of these components were studied. Finally, the method was used to determine sulphur dioxide in air samples on the highway in the Burdwan town. Formaldehyde was estimated in several synthetic mixtures.

INTRODUCTION

Sulphur dioxide and formaldehyde both are considered as air pollutants. A large number of reagents are known for spectrophotometric determination of these two species¹⁻⁶. Pararosaniline hydrochloride^{7,8} and *p*-aminoazo benzene^{9,10} are widely used for the determination of sulphur dioxide and formaldehyde on the basis of Schiff type reaction. In the present work a new reagent auramine (4, 4'-bis-dimethylaminobenzophenoneimide) has been successfully used for determination of these two compounds.

EXPERIMENTAL

Reagents: Sulphite solution: Sodium metabisulphite (E. Merck) was prepared in double-distilled water. The solution was prepared by the strength 1.05 M and the sulphite estimated titrimetrically¹¹

Formaldehyde solution: The solution was prepared by diluting 2 ml of 35–40% formaldehyde (E. Merck) solution in a 250 ml volumetric flask with double-distilled water and was standardized titrimetrically¹². The strength of the diluted solution was 0.94 M.

Auramine solution: Auramine (Veb, Germany) was recrystallized from water and dried in a vacuum desiccator. A stock solution (0.4 M) of the recrystallized reagent was prepared in 60% v/v aqueous ethanol.

All other reagents were of reagent grade and all aqueous solutions were made using double-distilled water.

Instrument: Absorbance was measured in a double beam UV-visible recording spectrophotometer (Beckman, model 26) equipped with matched 1 cm quartz cells.

Standard procedure for sulphur dioxide: In a small stoppered conical flask 2.5 ml of auramine solution (0.04 M), 2 ml of 11.5 M HCl were mixed and allowed to stand on a water bath (~60°C) for 10 min for discharging the colour of auramine and cooled at room temperature. Formaldehyde 0.2 ml of 0.94 M was then added to it. The resulting solution was transferred to a 25 ml volumetric flask. Two impingers, each containing 10 ml formaldehyde absorbing solution⁵, were connected in series. Quantitative amounts of sulphur dioxide was generated by an acidified solution of metabisulphite salt and the liberated gas passed through the impingers by the flow of purified air at 0.4 l/min. The flow rate was controlled by a rotameter and the air was drawn by a vacuum pump. An aliquot of sulphite solution containing 40.6–324.8 μg sulphur dioxide was used for standardizing the method. After sampling, the trapped sulphur dioxide solution was quantitatively transferred into a 25 ml volumetric flask containing the bleached reagent solution. The volume was then made up to the mark with double-distilled water. The resulting solution was allowed to develop its colour for 10 minutes. Finally, the absorbance was measured 15 minutes after colour development at 366 nm using a reagent blank as reference.

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Standard procedure for formaldehyde: In a stoppered conical flask the colour of 1 ml solution (0.04 M) of auramine was discharged by 0.8 ml HCl (11.5 M) by placing the mixture on a water bath (~60°C) for 10 min and was cooled at room temperature. Then 1 ml of 1.05 M sulphite solution and various amounts (0.2–2 ml) of standard formaldehyde solution ($9.43 \times 10^{-4} M$) were added and the solution was quantitatively transferred into a 10 ml volumetric flask. The volume was made up to the mark with double-distilled water and the resulting solution was allowed to develop its colour in 12 min. The absorbance was finally measured 15 min after colour development at 362 nm using a reagent blank as a reference.

RESULTS AND DISCUSSION

Absorbance curves and Beer's law range: The absorbance values of several aliquots containing known quantities of sulphur dioxide and formaldehyde were recorded in the wavelength range of 350 to 400 nm using a reagent blank. The λ_{\max} value of the resulting compound of sulphur dioxide, formaldehyde and auramine in the matrix employed for sulphur dioxide the analysis was 366 nm but in the matrix employed for formaldehyde it was 362 nm. Beer's law was obeyed over the ranges 0.08–8.12 ppm and 0.02–2.60 ppm for sulphur dioxide and formaldehyde determination respectively.

Sensitivity of the methods: According to Sandell¹³ the optimum concentration ranges were 1.50–5.30 and 0.47–1.67 ppm for sulphur dioxide and formaldehyde respectively. The corresponding Sandell sensitivity¹³ was $0.008 \mu\text{g cm}^{-2}$ sulphur dioxide and $0.002 \mu\text{g cm}^{-2}$ formaldehyde. The relative standard deviation values were $\pm 0.12\%$ and $\pm 0.07\%$. The confidence limits (95%) were 3.17 ± 0.10 ppm sulphur dioxide and 1.16 ± 0.02 ppm formaldehyde for 4 determinations in each case.

Effect of HCl concentration: The colour intensity of the product of sulphur dioxide, formaldehyde and auramine was varied with acid concentration. The variation of acid concentration to determine $32.00 \mu\text{g}$ sulphur dioxide and $9.75 \mu\text{g}$ formaldehyde per 10 ml solution was plotted against absorbance and it was found that maximum colour intensity and stability of the product were in the range of 0.57–1.15 M HCl.

Effect of reagent concentration: The variation of reagent concentration to determine 64 ppm sulphur

dioxide and 1.9 ppm of formaldehyde was studied at the optimum acid concentration range. The maximum colour intensity was developed in the range of 0.003–0.006 M auramine.

Effect of formaldehyde for determination of sulphur dioxide: 0.1 to 0.2 ml of 0.94 M formaldehyde was sufficient to determine 3.2 ppm sulphur dioxide in the optimum concentration range of acid and auramine as stated above.

Effect of sulphite for determination of formaldehyde: For 0.55 ppm formaldehyde, 1 ml of 1.05 M sulphite solution was sufficient for maximum colour development in the optimum reagent and acid concentration range. More than 2 ml of sulphite solution caused an error in the estimation.

Effect of foreign species: To determine formaldehyde and sulphur dioxide by this reagent, the effect of various foreign species was studied in both cases. The tolerance limits of different organic and inorganic substances are given in table 1 for the determination of 4.8 ppm of sulphur dioxide and 1.2 ppm formaldehyde. Only nitrite ion caused an interfer-

Table 1 Interferences and tolerable limits (in ppm) of other species in determination of sulphur dioxide and formaldehyde

Inorganic	ppm	Organic	ppm
Al(III)	100	Acetaldehyde	10
Ba(II)	100	Acetone	100
Ca(II)	100	Benzene	50
Cd(II)	50	Benzaldehyde	50
Co(II)	50	<i>o</i> -Dichlorobenzene	25
Cu(II)	50	Dimethylamine	25
Fe(III) ^a	50	Formic acid	25
Hg(II)	50	Phenol	50
Mg(II)	100	Toluene	50
Mo(II)	100	Urea	200
Ni(II)	100		
Zn(II)	200		
Br ⁻	200		
F ⁻	50		
NO ₃	200		
PO ₄ ³⁻	200		
SCN	100		
SO ₄ ²⁻	150		
Acetate	100		
Oxalate	50		
Tartarate	100		
Mg-EDTA	300		

^a In the presence of magnesium-EDTA.

Table 2 Determination of sulphur dioxide in air

Sample No.	Volume of air collected (litre)	Sulphur dioxide in air ($\mu\text{g}/\text{m}^3$)	
		Present method	Standard method
1	431.3	10.10	10.05
2	652.5	5.60	5.56
3	542.2	8.79	8.72
4	544.5	7.56	7.62
5	543.6	5.22	5.14
6	653.9	9.32	9.40
7	652.6	8.33	8.34
8	653.4	4.32	4.40

ence for both of these species and the interference was eliminated by adding urea¹⁴.

Collection and analysis of air samples: The present method was applied to analyse sulphur dioxide in air. The sample were collected from the highway, Burdwan town, West Bengal. Air was first drawn through a prefilter and then passed through two bubblers connected in series at 0.4 l/min. The bubblers contained 10 ml of absorbing solution in each. The height of the sampling station from the ground level was 3 m and was 4 m away from the highway. At regular intervals, the samples were collected for about 2 months. After sampling the absorbing solutions of the two impingers were mixed and made acidic with dilute HCl. Dissolved nitrogen dioxide which might be present was converted into nitrite was finally removed by urea¹⁴. The resulting solution was taken in a 25 ml volumetric flask and was made up to the mark with double-distilled water. A 10 ml aliquot was taken and analysed by the proposed method. The results are tabulated in table 2. The results of sulphur dioxide level in air samples by the standard method⁷ are also given in table 2.

Analysis of synthetic mixture: The proposed method for determination of formaldehyde was checked by analysing four synthetic mixture. The synthetic samples containing mixtures of (a) formaldehyde and different anions, (b) formaldehyde and different cations, (c) formaldehyde and different organic species, and (d) formaldehyde and different cations, anions as well as organic species were prepared. The results presented in table 3 indicate that this method is not affected by various species that might exist in the unknown samples.

Table 3 Analysis of formaldehyde in synthetic samples

Composition of the mixture (μg)	Formaldehyde found (μg)*	% Error
(a) HCHO-17, Br ⁻ -20, NO ₃ ⁻ -50, PO ₄ ³⁻ -25, SCN ⁻ -25, Oxalate-25.	17.1	+ 0.6
(b) HCHO-17, Ba(II)-25, Al(III)-25, Cu(II)-20, Zn(II)-25, Hg(II)-10.	17.2	+ 1.2
(c) HCHO-17, Acetaldehyde-5, Formic acid-5, Phenol-20, urea-50.	17.1	+ 0.6
(d) HCHO-17, Br ⁻ -20, NO ₃ ⁻ -50, Cu(II)-20, Zn(II)-25, Urea-50, Formic acid-5.	16.7	- 1.8

* Average of 2 determinations

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