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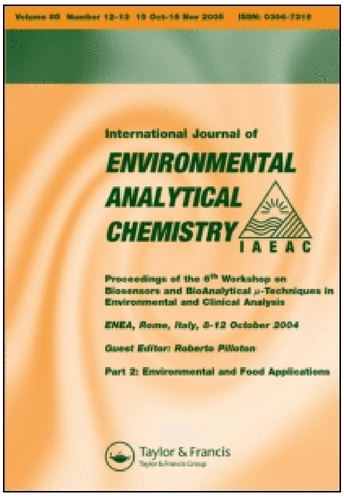

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Toxicology of Sulphur Dioxide and its Spectrophotometric Determination in Air Using a New Absorbing Agent

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An aqueous solution of malonyldihydroxamic acid is proposed for the absorption of atmospheric sulphur dioxide. The reagent has an absorption efficiency of ~100% and the resulting sulfite solution is stable for more than 30 days. The effect of variables for absorption of sulphur dioxide such as reagent concentration, flow rate and temperature has been investigated. The absorbed sulphur dioxide has been subsequently determined spectrophotometrically by *p*-aminoazobenzene-formaldehyde reagent in hydrochloric acid medium at optimized conditions. The pink coloured dye has a λ_{max} at 505 nm. The interference of nitrogen dioxide has been removed by use of sodium azide/oxalyldihydrazide. The proposed reagent is superior to TCM method in regard of manipulation, speedy results, use of stable and freely available pure and non-toxic reagents. The procedure has been applied for analysis of sulphur dioxide in vicinity of steel plant and work room air.

KEY WORDS: Sulphur dioxide, air, adsorption solution, malonyldihydroxamic acid.

INTRODUCTION

Sulphur dioxide, a well known air pollutant is emitted into the atmosphere in large quantities by chemical industries, traffic, petroleum refining, production of coke in steel plants, blast furnaces etc. [1–3]. The adverse effects caused by sulphur dioxide on animal life, plant life and human beings are well known 1[1–8]. The U.S. Environmental Protection Agency has recommended a maximum allowable limit of 0.03 ppm (daily exposure for 1 hour averaged over a year) and 0.14 ppm daily exposure for 8 hours, whereas the U.S. Occupational Safety and Health Administration (OSHA) has recommended a value of 5 ppm over an 8 hour exposure[4]. As SO_2 is important as a health hazard several methods have been reported for its trace detection and determination in ambient air. Almost all the methods employed for estimation of atmospheric sulphur dioxide have two stages, i.e. fixation and storage of sulphur dioxide from air in a suitable medium and its subsequent determination in the sample solution using a suitable reagent.

Tetrachloromercurate[9], aqueous iodine solution[10], hydrogen peroxide[11], glycerol alkali[12] and EDTA solution[13] have been reported in literature for the absorption of ambient sulphur dioxide. Terachloromercurate (recommended by West and Gaeke) the widely used absorbing medium for sulphur dioxide, suffers from major disadvantages such as oxidation of dichlorodisulfitomercurate II (1% decay per day at room temperature)[14] and the use of a relatively high concentration of expensive and toxic mercuric chloride. To overcome these drawbacks, modified West and Gaeke methods using formaldehyde[15] and triethanolamine[16] have been reported as absorbing reagents for sulphur dioxide. Formaldehyde is an efficient absorbing reagent but to achieve high absorption efficiency and stability, the pH of the solution must be maintained at 4 by phthalate buffer and the flow rate should be low. For the analysis of sulphur dioxide the complex has to be decomposed by addition of a base which makes the method tedious and in triethanolamine the stability of stored sulphur dioxide is only four days and triethanolamine itself is toxic.

Recently monoethanolamine[17] has been reported as an absorbing medium for sulphur dioxide by us. In search of still better absorbing medium for fixation and storage of atmospheric sulphur dioxide it was found that aqueous solution of malonyldihydroxamic acid (MDHA) can be employed for fixation and storage of atmospheric sulphur dioxide. The system is free from pH dependence and the absorbed sulphur dioxide is stable for more than 30 days. The reagent (MDHA) can be easily prepared, is pure, stable and non-toxic. The absorbed sulphur dioxide was determined later by using *p*-aminoazobenzene-formaldehyde reagent following the procedure of Kinseley and Throop[18]. (The reagent gives reproducible results and is available in pure form). The system has been optimized for sulphur dioxide determination. The absorption efficiency of the reagent is comparable to that of TCM, formaldehyde and monoethanolamine methods. The method has been applied to analysis of sulphur dioxide in the vicinity of steel plants.

EXPERIMENTAL

Apparatus

ECIL spectrophotometer Model GS 865 and Carl Zeiss spekol with 1 cm matched glass cells were used for spectral measurements. Fritted midget impingers (frit dia. 10 mm) of 35 ml capacity were used for air sampling. Flow calibrated rotameter with adjustable flow rate was used for air sampling.

Reagents

Preparation of Malonyldihydroxamic Acid (MDHA): 16.0 gms of diethylmalonate was added dropwise to the ammonical solution of 14 gms of hydroxylamine hydrochloride with vigorous shaking at 0°C. The white precipitate of MDHA was filtered and recrystallised twice with distilled water.

1) 0.5 M molar solution of MDHA and working standards were prepared by appropriate dilution.

2) *p*-Aminoazobenzene (0.02%) and formaldehyde (0.2%) solution were prepared as reported earlier[17].

3) Sodium sulphite solution: Sulphite solution containing 0.32 to 0.40 mg of sulphur dioxide/ml was prepared by dissolving 0.2 g of predried sodium sulphite in 250 ml distilled water. The sulfite solution was standardized iodometrically[19]. Working standards were prepared by appropriate dilution of the stock in MDHA (0.01 M).

4) Sodium Azide/Oxalyldihydrazide: 0.6% solution was freshly prepared.

Deionized deaerated water and analytical grade reagents were used.

Procedure

A. *Collection of Sample* Two midget impingers (35 ml capacity) each containing 10 ml of 0.01 M MDHA solution were connected in series to an air sampling train fitted with a rotameter. Air containing various concentrations of sulphur dioxide was passed through the impingers at a flow rate of 0.75 lit/min. 38.2 litres of air samples were collected and analysed later for sulphur dioxide[9]. No antifoaming reagent was used for the collection of sample.

B. *Analysis of Sample* After sampling, an aliquot (depending upon the concentration of sulphur dioxide) was transferred to a 25 ml volumetric flask, 1 ml of *p*-aminoazobenzene was added and acidity was adjusted by adding HCl to a concentration of 0.02 to 0.05 M. The 1 ml of formaldehyde solution and 1 ml of concentrated hydrochloric acid were added and filled up to the mark with distilled water. After 20 minutes the absorption of the pink coloured solution was measured at 505 nm against distilled water. The absorbance of the sample solutions was calculated by subtracting the absorbance value of reagent blank from the value of the sample.

The calibration curve was prepared by taking the aliquots of sodium sulphite solution in 0.01 M MDHA containing 0.1 to 1.0 ppm of sulphur dioxide in a final volume of 25 ml and developing the colour as described above. The concentration of sulphur dioxide was then calculated from the calibration curve.

RESULTS AND DISCUSSIONS

Absorbing efficiency of MDHA, stability of sulphur dioxide in MDHA, effect of time, temperature and aeration were taken into account to optimize the reaction condition. Generation of synthetic sulphur dioxide was done as reported earlier[17] but in this case the generation was done by taking a 5 μg/ml sulphur dioxide solution prepared in 0.01 M MDHA. It was found that generation of sulphur dioxide is quantitative. The data given in Table I shows the synthetic generation is reproducible and accurate.

Absorption efficiency

The absorption efficiency of MDHA was evaluated by sampling air

TABLE I

Reproducibility of the method for generation of sulphur dioxide and its determination

Flow rate = 0.75 lit/min.
Volume of air sampled in each case = 38.2 litres

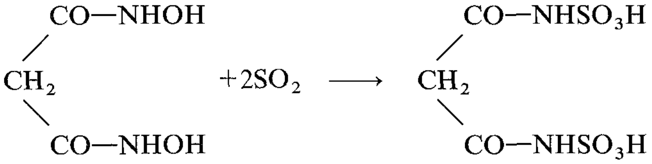
Set no.	Concentration of sulphur dioxide added μg	Concentration of sulphur dioxide found μg
1	2.5	2.48 ± 0.013
2	5.0	4.95 ± 0.040
3	7.5	7.46 ± 0.034
4	10.0	9.98 ± 0.022
5	12.5	12.47 ± 0.0175
6	15.0	14.99 ± 0.014
7	17.5	17.47 ± 0.038
8	20.0	19.98 ± 0.048
9	25.0	24.99 ± 0.018

Mean of 6 repetitive analysis.

containing 2.5 μg to 1275 μg of sulphur dioxide for various lengths of time and at different flow rates. Samples containing higher concentration of sulphur dioxide were diluted appropriately with distilled water prior to the analysis. In such cases the reagent blank (i.e. solution of the second impinger) was also diluted accordingly. Almost 100% absorption was achieved in the first impinger. The second impinger gave a negative test for sulphur dioxide. The different concentration of MDHA solutions i.e. 0.005 to 0.15 M MDHA had no effect on absorption efficiency. Flow rate variation from 0.25 lit/min to 2 lit/min and temperature variation from 15° to 40°C did not effect the absorption efficiency.

Stability of sulphur dioxide collected samples

The sulphite solution prepared in MDHA was found to be stable for 30 days at room temperature. No effect of aeration in absorbed samples was observed. The probable reaction involved in the fixation of sulphur dioxide as aminosulphonic acid in MDHA can be represented as follows:



$$\mathrm{CH_2}\left\langle\begin{array}{l}\mathrm{CO{-}NHOH}\\ \mathrm{CO{-}NHOH}\end{array}\right. + 2\mathrm{SO_2} \longrightarrow \mathrm{CH_2}\left\langle\begin{array}{l}\mathrm{CO{-}NHSO_3H}\\ \mathrm{CO{-}NHSO_3H}\end{array}\right.$$

(I) Malonyldihdroxamic Acid

(II) Aminosulphonic Acid

The sulphur dioxide absorbed in MDHA is released by addition of 2 drops of 0.2% HCl. The released sulphur dioxide combines *in situ* with *p*-aminoazobenzene in presence of formaldehyde to give a pink colour dye having $\lambda_{\max}$ 505 nm.

The mechanism of the reaction is similar to that proposed earlier[15,20] i.e. formation of aminomethane sulphonic acid. The *p*-aminoazobenzene containing only one amino group has been preferred over *p*-rosaniline because it is more sensitive and gives a dye of known structure.

Effect of variables on colour development

The order of addition of reagents to the absorbed sulfurdioxide solution in MDHA was investigated. The order of addition for maximum colour development was *p*-aminoazobenzene, formaldehyde and hydrochloric acid. After addition of *p*-aminoazobenzene the best results were obtained at a HCl concentration of 0.06 to 0.20 M. After addition of formaldehyde solution maximum colour development was found to take place between 0.2–1.5 M hydrochloric acid. This is in agreement with earlier reported method. In the present method the acidity was maintained at 0.1 M and 0.8 M hydrochloric acid after addition of *p*-aminoazobenzene and formaldehyde respectively to the MDHA solution containing absorbed sulphur dioxide solution. In the earlier method 10 minutes were required for full colour development and the product was stable for an hour. In this method the full colour development takes 15 minutes but the product is stable for 12 hours which is an added advantage of the method.

Beer's Law and reproducibility

Beer's Law was found valid between 2.5 to 25 μg/25 ml of sulphur dioxide in 0.01 M MDHA solution. The method was found to be reproducible. The standard deviation and relative standard deviation for 20 μg of sulphur dioxide in 25 ml solution were found to be ±0.048 and ±0.24% respectively.

Effects of foreign species

To assess the applicability of the method, effect of foreign ions on the determination of sulphur dioxide was studied. The effect of Fe(III), Cu(II), V(V), Mn(II) and Cr(III) which are known to catalyse the aerobic oxidation of sulphite ion was studied by adding 500 μg of each to 15 μg of sulphur dioxide in 25 ml solution. No significant change in absorbance was observed except in case of V(V). More than 200 μg of V(V) if present was found to interfere with the method as V(V) forms a violet coloured complex with MDHA.

Effect of nitrogen dioxide, a common interferent in the determination of atmospheric sulphur dioxide was also studied. Nitrite ion added directly to the absorbing medium caused interference. It was observed that addition of 2 ml of 0.6% solution of oxalyldihydrazide directly to the absorbing solution gave 2 to 3% low results. It may be due to the fact that there is no stoichiometric conversion of nitrogen dioxide to nitrite ion in presence of oxalyldihydrazide. Studies carried out show that when generated nitrogen dioxide was passed through oxalyldihydrazide solution, no nitrite ion was formed. Thus the interference of nitrogen dioxide can be eliminated by passing the air through 10 ml of 0.6% solution of oxalyldihydrazide first. Similar studies carried out by using sodium azide solution gave 5 to 6% low results whereas the use of sulphamic acid gave 10 to 15% low results as observed by earlier workers[9,10]. Results are given in Table II. Hydrogen sulphide if present can be eliminated as reported earlier[17]. Other gases such as ammonia, chlorine, halogen acids, do not interfere. Effect of ozone could not be studied due to this nonavailability.

TABLE II
Interference of nitrogen dioxide
Volume of air passed per determination = 38.2 litres

Amount of sulphur dioxide taken μg	Amount of nitrogen dioxide taken μg	Elimination by	Absorbance 505 nm
5	—	—	0.125
	50	—	—
	50	a	0.110
	50	b	0.125
	100	a	0.100
	100	b	0.120
	250	b	0.125
	500	b	0.120
	1000	b	0.115
10	—	—	0.250
	50	—	—
	50	a	0.220
	50	b	0.250
	100	a	0.200
	100	b	0.245
	250	b	0.245
	500	b	0.240
	1000	b	0.240
20	—	—	0.505
	50	—	—
	50	a	0.445
	50	b	0.500
	100	a	0.430
	100	b	0.495
	250	b	0.490
	500	b	0.470
	1000	b	0.470

[a] Sulphur dioxide and nitrogen dioxide are bubbled through a tube containing 0.6% sulphamic acid.
[b] Sulphur dioxide and nitrogen dioxide are bubbled through a tube containing 0.6% oxalyldihydrazide.

Application of the method in the determination of atmospheric sulphur dioxide

To check the validity of the method a comparative study of the method with that of West and Gaeke method was done. Two sets of fritted midget impingers were connected in two series one set containing 10 ml of 0.01 MDHA solution and the second set containing 10 ml of 0.04 M TCM solution as absorbing medium, respectively. 38.2 litres air containing different concentration of SO_2 were passed through these solutions. The MDHA solution as well as TCM solution were analysed after sampling by the recommended procedure. In both cases no significant increase in blank was observed. The coefficient of correlation of the two methods was found to be 0.999.

Analysis of atmospheric sulphur dioxide in the vicinity of steel plant near Raipur as well as in the laboratory (where artificial sulphur dioxide was created by burning sulphur) was done by both West and Gaeke method and the proposed method[9]. The analytical values obtained are comparable. The procedure is as follows.

1) Air sampling train fitted with a rotameter was arranged near the plant and to this two midget impingers were connected in two series, one set containing 0.04 M TCM solution and the other set containing 0.01 M MDHA solution. 38.2 litres of air were drawn through the absorbing solution at a flow rate of 0.75 lit/min., for various lengths of time and at different places around the plant. The sulphur dioxide content in TCM solution was estimated using *p*-rosaniline by West and Gaeke method and sulphur dioxide in MDHA was estimated as recommended in procedure.

The concentration of sulphur dioxide present in air was calculated by the earlier reported method[9].

2) Artifical sulphur dioxide atmosphere was created by burning 0.1 gm of sulphur in the laboratory. Air sampling measurement of sulphur dioxide was done as described above. In both the cases analytical values obtained by West and Gaeke were compared with those obtained by present method (Table III) and almost identical values were obtained. To check the results precisely standard addition of SO_2 was done.

Since the method is simple and rapid, it can be satisfactorily employed for the measurement of sulphur dioxide.

CONCLUSION

Stability of sulfite solution in the present system is superior to the West and Gaeke method. The system is free from pH dependence. Oxidizing agents as Fe(III), Cr(III), Mn(II), Cu(II) abd V(V) do not interfere with the method. *p*-Aminoazobenzene used for colour development has an added advantage in terms of simplicity allowable acidity range, reproducibility and stability of raction product over the West and Gaeke method[9].

TABLE III

Analysis of sulphur dioxide in vicinity of steel plant and work room air[a]

Flow rate = 0.75 lit/min
Volume of air sampled = 38.2 litres

Vicinity of steel plant	Sulphur dioxide obtained[b] West and Gaeke Method µg	Sulphur dioxide obtained proposed method µg
S_1	12.25	12.31
S_2	7.56	7.51
S_3	2.01	2.03
S_4	0.52[c]	0.53[c]
S_5	0.31[c]	0.32[c]
S_6	20.65	20.70
S_7	31.26	31.24
S_8	5.58	5.56
S_9	4.29	4.30
Work room air		
1	125.60	125.70
2	82.50	82.80
3	40.10	40.20

[a] The concentration of sulphur dioxide was calculated by applying the formula:

$$SO_2,\ \text{ppm} = \frac{(A - A_0)\,0.382B}{V}$$

where A is the sample absorbance; A_0 is the blank absorbance; 0.382 is the volume (µl) of 1 µg SO_2 (at 25°C) 760 mm Hg; B is the calibration factor × 25 ml (µg/A unit); V is the sample volume in litres corrected at 25°C, 760 mm Hg.

[b] Absorption/sampling of sulphur dioxide from 8 different spots around the steel plant near Raipur was done.

[c] Standard addition method was applied.

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