CHAPTER VII

Sulphur Dioxide

Colorimetric Determination of Sulphur Dioxide & Sulphites in Various Environmental Samples.
COLORIMETRIC DETERMINATION OF SULPHUR DIOXIDE AND SULPHITES IN VARIOUS ENVIRONMENTAL SAMPLES.

SUMMARY

Rhodamine-B has been proposed as a simple and sensitive colorimetric reagent for the estimation of sulphur dioxide in air. The air sample containing sulphur dioxide is passed through the absorbing solution of aqueous potassium iodate and N-chlorosuccinimide to liberate iodine. The liberated iodine bleaches the pinkish red coloured rhodamine - B dye, which measured at 555nm. Beer's law was obeyed in the range of 0.5-5.0 µg of sulphite per 25-ml (0.02-0.2ppm) equivalent to 0.4-4.0 µg of sulphur dioxide (0.016-0.16 ppm). The molar absorptivity and Sandell's sensitivity were found to be 4.56 x10^5 mol^-1 cm^-1 and 0.00017 µg cm^-2 respectively. The method has been suitably modified and successfully applied to the determination of sulphites in water after liberation of sulphur dioxide in acidic medium.
INTRODUCTION

Sulphur dioxide is one of the most widely distributed air pollutants. It is a colourless non-inflammable gas with a suffocating odour (1). The auto-exhaust, roasting of sulphite ores, steel industry, thermal power plant and fertilizer plant generate large quantities of sulphur dioxide (2), when sulphur containing substances such as coal, fuel oil, gasoline are combusted and sintering of sulphur containing fine ores also emit sulphur dioxide (3,4). It is expected that about 109 million tonnes of sulphur dioxide be added every year into the global environment (5). It is introduced into the environment via its application as a bleaching agent, preservatives, fungicides, and coolants in refrigerators, extractants in the petroleum industry and pharmaceuticals (6-8).

Sulphur dioxide is a strong irritant, which can be perceived by its odour and taste even when highly diluted (9). On inhalation it causes sorethroat, chest pain, bronchitis, intense irritation to eyes, mucous membranes and respiratory tract (10,11). It forms complexes with Fe (III) and Cu (II) both in solution and solid form which destructively attacks the disulphide bonds in proteins leading to respiratory failure (12). It is a clastogenic and genotoxic agent and is also suspected to cause mutagenic effects and several types of lung disease (13). Highly acidic rainfall and elevated levels of atmospheric sulphur dioxide severely damage crops, forests and building materials (14,15). It increases the soil acidity making its unsuitable for plant growth. Cytogenic effect of sulphurdioxide on cytotypes of solanum nigrum complex has been reported recently (16).

USEPA has recommended maximum allowable limit of 0.01 ppm for daily exposure for one-hour duration and 0.14 ppm for daily exposure for 3 hrs at home. (17). 5 ppm reduced to 2 ppm is the permissible exposure limit value for 8 hrs. duration (18). The threshold levels of sulphur dioxide injury in plant are quite
low as compared to man and animals as shown in following table. 
Sulphurdioxide concentration producing threshold injury (5)

<table>
<thead>
<tr>
<th>Category</th>
<th>Short term exposure one hour / day (ppm)</th>
<th>Long term exposure one hour / day (ppm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Plants</td>
<td>0.5 - 2.0</td>
<td>0.01 - 0.05</td>
</tr>
<tr>
<td>Man</td>
<td>0.5 - 3.0</td>
<td>0.02 - 0.10</td>
</tr>
<tr>
<td>Animals</td>
<td>1.0 - 4.0</td>
<td>0.05 - 0.20</td>
</tr>
</tbody>
</table>

Sulphite is one of the common oxidised form of sulphur. It is largely used in bleaching, food preservation, textile, photography, and pulp and paper industries (19). It is also toxic for human beings with effects which include anxiety, nausea, eye strain, headache, asthma and depresses the central nervous system (20). Sulphite reduces the dissolved oxygen content and chemical oxygen demand of water, which is harmful for aquatic species (21).

The wide occurrence and toxicity on all living beings, suitable and sensitive analytical methods are required for its determination in the environmental samples. Several instrumental methods such as AAS (22), GC-MS (23), FT-IR (24), GC(25,26), FIA (27,28), amperometric (29), HPLC (30), UVS (31), gold film sensor (32), fluorescence photometric (33) and a large number of spectrophotometric methods (34-37) are available in literature. Some methods are based on iodometric titration but they are less sensitive and interference from organic and other reduced compound (38). Colorimetric methods are also reported for the determination of sulphites as sulphur dioxide (39,40). These methods involve the use of different reagents such as tetrachloromercurate (41), buffered formaldehyde (42), morpholine (43) and parasosaniline, monoethanolamine (44), semicarbazide (45) hydroxamic acid (46) and p-aminoazobenzene, potassium iodate, N-chlorosuccinimide and leucocystal violet (LCV) (47) are developed as indirect method for determination of sulphur dioxide liberated from acidified sulphite solution. Some other indirect methods are also reported on the above principle (48).
Here a simple sensitive and selective method using a common laboratory reagent rhodamine - B has been reported. The present method is based on the liberation of iodine by reaction between absorbing solution (Potassium iodate + NCS + water) and sulphur dioxide from the acidified solution of sulphites. The liberated iodine bleaches rhodamine - B that is measured at 555 nm. Beer's law range is 0.5-5.0 µg of sulphite per 25 ml (0.02-0.2 ppm). The method is applied for the determination of sulphur dioxide and sulphite in air and water respectively.

EXPERIMENTAL

Apparatus

A Systronics 106 digital spectrophotometer and a Systronics 335 digital pH meter were used. For air sampling midget impinger of 35 ml capacity were used and flow rate was controlled by rotameter.

Reagents

All chemicals used were of A R grade or the best quality available. Double distilled deionised water was used throughout the experiment.

Sodium sulphite solution

300 mg of sodium sulphite was dissolved in 500 ml of water and standardised by iodometry. The working standard was prepared from appropriate dilution of the fresh stock solution in aqueous 0.005 M-oxalidihydroxamic acid (ODHA). The solution of sulphurdioxide in ODHA are stable for a long time (49).

Rhodamine - B (Stuttgart, W. Germany)

0.05% aqueous solution was used.

Potassium iodate (E. Merck)

0.1 N-aqueous solution was prepared and stored in amber coloured bottle.
**N - Chlorosuccinimide (NCS - Aldrich)**

500 mg NCS in a 500 ml volumetric flask containing 5 g of succinimide, 50 ml water was added to dissolve the solid and the solution was finally diluted to 500 ml with water.

**Hydrochloric acid**

6M solution was used.

**Absorbing solution**

7 ml of potassium iodate and 1 ml of NCS solution diluted to 10 ml with distilled water.

**PROCEDURE**

An aliquot of working standard solution containing 0.5 - 5.0 µg of sulphite was taken in an impinger. Sulphur dioxide was liberated from the aliquot by adding 5 ml of 6 M-hydrochloric acid dropwise from a microburette. The liberated sulphur dioxide was absorbed in the absorbing solution taken in two midget impingers 35 ml capacity each containing 10 ml of absorbing solution connected to a source of suction. The air was passed through the solution at a rate of 1 L/min for 30 min. After that the sampling of solutions of the two impingers were mixed and 1 ml of rhodamine - B was added to it and shaken for two min. the volume was made up to 25 ml by adding distilled water. The solution was kept for 15-20 min. for the reaction to complete. Then the absorbance of the final solution was measured at 555 nm against the reagent blank.

**Determination of sulphur dioxide in air**

The method has been successfully applied for the determination of sulphur dioxide in the vicinity of a steel plant and as well as in the laboratory air, where artificial sulphur dioxide was liberated by burning 0.1 g of sulphur powder.
An air sampling train was fitted near steel plant and in laboratory. In this two impingers containing 10 ml of absorbing solution was connected to a source of suction. The air was sampled at the rate of 1 L/min for 30 min. The aliquots of absorbing solution were then analysed by the present and the reported method (41). The sulphur dioxide concentrations determined by both the methods were found to be in good agreement. The results are shown in Table - 1.

**Determination of Sulphite**

*In demineralized water (Ranboxy Fine Chemical Ltd.)*

Demineralized water samples were analysed for sulphites. They tested negative to these samples known amount of sulphite (2.0, 2.5 and 3.0 μg) was added and analysed by the present and reported method (41) with excellent recoveries 98-99% (Table - 2).

*In polluted water*

Sulphites are reported to be used as preservatives in food and soft drink industries (50-52). Known amount of the polluted water samples from those industries were collected and filtered. The filtrate was analysed by the present and the reported method (41) (Table - 2).

*In photographic waste water -*

The photographic wastewater contains silverbromide, sodium thiosulphate and metabisulphite. This waste was diluted hundred times. 1 ml of these wastewater taken and formic acid was added for removal of bromide. Then it was treated with few drop of 1 % barium chloride for precipitation of silver. After filtration, the filtrate was analysed by the present and the reported method (41) (Table - 2).
RESULTS AND DISCUSSION

Absorption spectra

The absorption spectra of the rhodamine-B dye showed a maximum absorption in reagent blank gave at 555 nm (Fig. 1)

Adherence to the Beer's Law, Molar absorptivity and Sandell's sensitivity

Beer's law is obeyed over the concentration range 0.5 - 5.0 µg of sulphite per 25 ml of the final solution (0.02-0.2 ppm) equivalent to 0.4 - 4.0 µg of sulphur dioxide (0.016 - 0.16). The molar absorptivity and Sandell's sensitivity were found to be $4.56 \times 10^5$ mol$^{-1}$ cm$^{-1}$ and 0.00017 cm$^{-2}$ respectively (Fig - 2).

Effect of reagent concentration

The maximum absorbance were obtained when dropwise addition of 5 ml of 6M hydrochloric acid was sufficient for generating sulphur dioxide from sulphite solution taken in an impinger connected to an air sampling train. It was effectively absorbed in an absorbing solution and 1 ml of 0.05% rhodamine - B was sufficient for colour reaction. The bleached colour was found to be stable for several days. As the quantity of rhodamine - B and absorbing solution were increased the absorbance of the solution remained constant (Fig - 3).

Effect of time, temperature and pH

The colour reaction was carried out at room temperature (27°C) and time period of 15-20 min. was necessary for the completion of the reaction. The final absorbance was not affected by change in pH value or time period. It has been observed that there was linearity in absorption value in the pH range of 1-6. However all the reactions are carried out at pH 1.5 – 2.0 (Table - 3).

Reproducibility

Reproducibility of the method was accessed by analysis 2.5 µg of sulphite
per 25 ml for a period of seven days. The standard deviation and relative standard deviation were found to be 0.0069 and 1.54% respectively.

Effect of foreign species

The effect of foreign species on the determination of sulphur dioxide and sulphite were studied. Removal of nitrogen dioxide and nitrite by addition of a few drops of sodium azide before liberation of sulphur dioxide was performed. Carbon dioxide, carbon monodioxide and ammonia present in air and nitrate, carbonate, sulphate, phosphate, chloride, formaldehyde present in water did not interfere with the colour reaction. The tolerance limit value for some species are given in table - 4.

Colour reaction (Scheme - A)

The colour reaction involves following steps.

1. Sulphur dioxide is passed through the absorbing solution of aqueous potassium iodate and N-chlorosuccinimide to liberate iodine.
2. Liberated iodine bleaches the pinkish red colour of rhodamine - B dye.

APPLICATION

To check the validity of the method it has been applied for the determination of sulphur dioxide in air and sulphite in different water samples. The results obtained were compared with reported method (41) and are shown in table - 1 and 2.

CONCLUSION

The present method has been compared with other spectrophotometric methods found to be simple, sensitive and selective. This method in good alternative to some reported methods (Table - 5) and its advantages are mainly due to cheaper cost, easier availability of the reagent and higher stability of colour for rhodamine - B dye.
Scheme - A  Colour reaction of sulphur dioxide

1. \[ \text{Na}_2\text{SO}_3 + 2\text{HCl} \rightarrow 2\text{NaCl} + \text{H}_2\text{O} + \text{SO}_2 \uparrow \]

2. \[ \text{NCS} \rightarrow \text{NH}_4\text{Cl} + 2\text{KIO}_3 + 4\text{SO}_2 + 4\text{H}_2\text{O} \]

3. \[ \text{Et}_2\text{NH} \text{COOH} \rightarrow \text{Et}_2\text{N} \text{CO} \text{Et}_2 \]

\[ + \text{I}_2 \xrightarrow{\text{Oxidation}} \text{Rhodamine - B dye} \]

(Quinonoid form)

Pinkish red colour

\[ \lambda_{\text{max}} 555 \text{ nm} \]

\[ \xrightarrow{+e} \text{Bleached dye} \]

(Benzenoid form)
**Fig -1**  *Absorption spectra of the dye*

A - Concentration of sulphite in 2.5 µg / 25 ml.
B - Reagent blank

**Fig -2**  *Calibration curve for determination of sulphur dioxide*

Absorbance 555 nm vs Concentration in µg / 25 ml.
Fig -3  
Effect of reagent concentration on colour reaction
Concentration of sulphite in 2.5 μg / 25 ml.

Amount of rhodamine - B in ml - B

Absorbance 555 nm

Amount of abosorbing solution in ml - A

(KIO₃ + NCS + H₂O)
### Table 1: Determination of sulphur dioxide in the vicinity of the steel plant and ambient air

<table>
<thead>
<tr>
<th>Sample volume or mass (1 L/min for 30 min)</th>
<th>Total sulphur dioxide found (µg)</th>
<th>Present method</th>
<th>Reported method (41)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Viscinity of the Steel plant (S-1)</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>(S-1)</td>
<td>3.90</td>
<td></td>
<td>3.85</td>
</tr>
<tr>
<td>(S-2)</td>
<td>2.89</td>
<td></td>
<td>2.83</td>
</tr>
<tr>
<td>(S-3)</td>
<td>1.41</td>
<td></td>
<td>1.36</td>
</tr>
<tr>
<td>Ambient air</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>(A)</td>
<td>2.83</td>
<td></td>
<td>2.83</td>
</tr>
<tr>
<td>(B)</td>
<td>2.50</td>
<td></td>
<td>2.45</td>
</tr>
<tr>
<td>(C)</td>
<td>2.12</td>
<td></td>
<td>2.07</td>
</tr>
</tbody>
</table>

### Table 2: Determination of sulphite in demineralized, polluted and photographic waste water by the present and reported method (41)

<table>
<thead>
<tr>
<th>Sample volume or mass</th>
<th>SO$_2$ originally found (µg)</th>
<th>SO$_2$ added (µg)</th>
<th>Total SO$_2$ found * (µg)</th>
<th>% of recovery</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Present method</td>
<td>Reported method</td>
<td>Present method</td>
<td>Reported method</td>
</tr>
<tr>
<td>Demineralized water (5 ml)</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>(A)</td>
<td>-</td>
<td>2.0</td>
<td>1.98</td>
<td>99.0</td>
</tr>
<tr>
<td>(B)</td>
<td>-</td>
<td>2.5</td>
<td>2.46</td>
<td>98.4</td>
</tr>
<tr>
<td>(C)</td>
<td>-</td>
<td>3.0</td>
<td>2.94</td>
<td>98.0</td>
</tr>
<tr>
<td>Polluted water (5 ml)</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>(A)</td>
<td>0.93</td>
<td>2.0</td>
<td>1.89</td>
<td>98.6</td>
</tr>
<tr>
<td>(B)</td>
<td>1.21</td>
<td>2.0</td>
<td>3.16</td>
<td>98.4</td>
</tr>
<tr>
<td>(C)</td>
<td>1.39</td>
<td>2.0</td>
<td>3.35</td>
<td>98.8</td>
</tr>
<tr>
<td>Photographic waste water (1 ml)</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>(A)</td>
<td>3.63</td>
<td>-</td>
<td>3.56</td>
<td>98.0</td>
</tr>
<tr>
<td>(B)</td>
<td>3.71</td>
<td>-</td>
<td>3.65</td>
<td>98.3</td>
</tr>
<tr>
<td>(C)</td>
<td>3.82</td>
<td>-</td>
<td>3.78</td>
<td>98.9</td>
</tr>
</tbody>
</table>

*Mean of three replicate analyses
### Table 3
**Effect of time period on absorption value.**
Concentration of sulphite in 2.5 μg / 25ml.

<table>
<thead>
<tr>
<th>S.No.</th>
<th>Time period</th>
<th>Absorption value</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>5</td>
<td>0.458</td>
</tr>
<tr>
<td>2</td>
<td>10</td>
<td>0.456</td>
</tr>
<tr>
<td>3</td>
<td>15</td>
<td>0.457</td>
</tr>
<tr>
<td>4</td>
<td>20</td>
<td>0.456</td>
</tr>
<tr>
<td>5</td>
<td>25</td>
<td>0.455</td>
</tr>
<tr>
<td>6</td>
<td>30</td>
<td>0.454</td>
</tr>
<tr>
<td>7</td>
<td>35</td>
<td>0.456</td>
</tr>
</tbody>
</table>

### Table 4
**Effect of foreign species**
Concentration of sulphite in 2.5 μg / 25 ml = 0.1 ppm

<table>
<thead>
<tr>
<th>Foreign species</th>
<th>Tolerance limit* (ppm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ca²⁺, Ba²⁺, Sr²⁺</td>
<td>2200</td>
</tr>
<tr>
<td>Fe³⁺, Cr³⁺, Bi³⁺</td>
<td>1300</td>
</tr>
<tr>
<td>NO₃⁻</td>
<td>700</td>
</tr>
<tr>
<td>PO₄³⁻, SO₄²⁻, CO₃²⁻</td>
<td>500</td>
</tr>
<tr>
<td>Al³⁺, Cu²⁺</td>
<td>400</td>
</tr>
<tr>
<td>Cl⁻, Br⁻, F⁻, CN⁻</td>
<td>250</td>
</tr>
<tr>
<td>V⁵⁺, Pb¹⁺²</td>
<td>100</td>
</tr>
<tr>
<td>Hg²⁺, Mn⁺²</td>
<td>50</td>
</tr>
</tbody>
</table>

* Tolerance limit may vary the absorbance by ±2%
<table>
<thead>
<tr>
<th>S.N.</th>
<th>Absorbing solution for SO₂</th>
<th>Chromogen</th>
<th>Beer's law range (ppm)</th>
<th>Remarks</th>
</tr>
</thead>
<tbody>
<tr>
<td>01</td>
<td>Tetrachloromercurate (41)</td>
<td>Pararosaniline</td>
<td>0.0-1.4</td>
<td>Use hazardous mercury II salts</td>
</tr>
<tr>
<td>02</td>
<td>Buffered formaldehyde (42)</td>
<td>Pararosaniline</td>
<td>0.0 - 1.4</td>
<td>Use costly PRA</td>
</tr>
<tr>
<td>03</td>
<td>Morpholine (43)</td>
<td>Pararosaniline</td>
<td>0.02 - 0.5</td>
<td>Highly toxic reagents used</td>
</tr>
<tr>
<td>04</td>
<td>Monoethanolamine (44)</td>
<td>P-aminoazo-benzene</td>
<td>0.8 - 8.0</td>
<td>Less sensitive</td>
</tr>
<tr>
<td>05</td>
<td>Semicarbazide (45)</td>
<td>P-aminoazo-benzene</td>
<td>0.1 - 1.2</td>
<td>NO₂ interfere above 8 ppm</td>
</tr>
<tr>
<td>06</td>
<td>Hydroxamic acid (46)</td>
<td>P-aminoazo benzene</td>
<td>0.12 - 1.24</td>
<td>H₂S interfere</td>
</tr>
<tr>
<td>07</td>
<td>Potassium iodate and N- chlorosuccinimide (47)</td>
<td>Leuco crystal violet (LCV)</td>
<td>0.01 - 0.08</td>
<td>Sensitive but extractive used costly LCV</td>
</tr>
<tr>
<td>08</td>
<td>Potassium iodate and N- chlorosuccinimide (Present method)</td>
<td>Rhodamine-B</td>
<td>0.02 - 0.2</td>
<td>Sensitive, selective free from various interference and cheaper common laboratory reagent used.</td>
</tr>
</tbody>
</table>
REFERENCES