Spectrophotometric Determination of Sulfur Dioxide in Air, Using Thymol Blue

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A simple and sensitive spectrophotometric method was developed for the determination of trace amounts of sulfur dioxide. The method is based on the reaction of SO₂ with a known excess of ICl as the oxidant. The unreacted ICl iodinates thymol blue under acidic conditions. The λₘₐₓ of thymol blue is at 545 nm under acidic conditions, and on iodination λₘₐₓ shifts to 430 nm. This shift results in a decrease in the absorbance at 545 nm. The amount of uniodinated thymol blue present depends on the concentration of unreacted ICl, which in turn depends on the SO₂ concentration. The system obeys Beer’s law in the range 0–30 μg SO₂ in a final volume of 25 mL, having a molar absorptivity of 3.2 × 10⁴ L/mol·cm with a relative standard deviation (RSD) of 2% at 24 μg SO₂ (n = 10). The uniodinated dye can be extracted into 5 mL isoamyl alcohol under acidic conditions for measurement of absorbance. The extraction method obeys Beer’s law in the range 0–5 μg SO₂, having a molar absorptivity of 4.16 × 10⁴ L/mol·cm with an RSD of 1.9% at 4 μg SO₂ (n = 10). The method has been successfully applied to the determination of atmospheric SO₂.

Sulfur dioxide is one of the major air pollutants causing environmental concern in recent decades. It is widely used as an antioxidant in the pharmaceutical industry, as a bleaching agent in the pulp and paper industries (1), and as a food preservative and refrigerant (2). The main sources of SO₂ in the atmosphere are volcanic emissions and the combustion of coal and oil. It is a major contributor in the formation of acid rain (3). With the growing concern over sulfur dioxide as an important gaseous pollutant, reliable methods for its determination are continuously being sought. Methods involving spectrophotometry (4), chemiluminescence (5), and fluorimetry (6) have been developed for the determination of SO₂. The present paper describes a simple and sensitive procedure for the determination of atmospheric sulfur dioxide, based on the reaction of SO₂ with ICl. The reliability of the method was established by parallel determinations using the West and Gaeke method (7).

Experimental

Apparatus

(a) Spectrophotometer with 1 cm glass cells.—To measure absorbance values; Carl Zeiss PMQ II (Germany).
(b) Fritted glass bubblers with suitable suction devices.—For trapping SO₂ from the air.
(c) Rotameter.—To measure the flow rate of air.

Reagents

(a) Trapping solutions.—(1) Triethanolamine (1.5%).—Prepared by dissolving 15 g triethanolamine (specific gravity, 1.124) in 1 L water. Air can be sampled at a rate of 0.5–1.5 L/min.
(2) Citrate–NaOH.—Prepared by dissolving 2.94 g trisodium citrate in 0.1N NaOH and diluting to volume with 1N NaOH. Air can be sampled at a rate of 0.2–0.5 L/min.
(3) Buffered formaldehyde.—Prepared by buffering 7mM formaldehyde at pH 4.76, using sodium acetate–acetic acid solution. Air can be sampled at a rate of 0.4–0.7 L/min.
(4) Glycerol–NaOH.—Prepared by dissolving 5 g glycerol in 0.1N NaOH and diluting to 100 mL with 0.1N NaOH. Air can be sampled at a rate of 0.4 L/min.
(b) Standard sulfur dioxide solution.—Prepared by dissolving 0.22 g anhydrous sodium sulfite in 500 mL water and standardizing iodimetrically (8). The sulfur dioxide content of this solution is 200 μg/mL. Suitable volumes of this solution were diluted with the respective trapping solutions to obtain solutions containing sulfur dioxide at 6 and 1 μg/mL.
(c) Iodine monochloride (ICl).—Prepared by dissolving 0.28 g KI, 0.18 g KIO₃, and 50 g NaCl in 400 mL water. The solution was cooled, and 75 mL concentrated H₂SO₄ was added. The solution was cooled, diluted to 500 mL with water (9), and standardized iodometrically. Prepared ICl solution was found to be 0.0047M in 5.4N H₂SO₄. A 4.3 mL aliquot of the prepared stock solution was diluted to 100 mL with 4.5N H₂SO₄ to obtain 2 × 10⁻⁴M ICl (solution A) with an overall acidity of 4.54N with respect to H₂SO₄. A 25 mL aliquot of solution A was placed in a 100 mL volumetric flask and diluted to volume with 4.50N H₂SO₄ to obtain 5 × 10⁻⁵M ICl. The prepared stock solution was found to be stable for 2 months.
(d) Thymol blue.—Prepared by dissolving 0.01 g thymol blue in 0.1N NaOH, and diluting to 100 mL with 0.1N NaOH.

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Figure 1. Absorption spectra measured against water: (A) reagent blank; (B) 12 μg SO₂; and (C) 30 μg SO₂. Absorption spectra measured against isoamyl alcohol: (A’) reagent blank; (B’) 12 μg SO₂; and (C’) 5 μg SO₂.

\[
\begin{align*}
2 \text{ICl}^- & \rightarrow 2 \text{ICl} + 2\text{Cl}^- \\
\text{SO}_2 + 2\text{ICl} + 2\text{H}_2\text{O} & \rightarrow \text{I}_2 + \text{SO}_4^{2-} + 4\text{H}^+ + 2\text{Cl}^-
\end{align*}
\]

Figure 2. Reaction scheme showing the iodination of thymol blue.
16 mL 0.01% thymol blue solution was diluted to 100 mL with 0.1N NaOH (0.0016%).

**Construction of Calibration Graph**

(a) *Aqueous procedure.*—To a series of 25 mL standard flasks containing 5 mL 2·10⁻⁴ M ICl in 4.5N H₂SO₄ was added 10 mL trapping solution containing 0–30 mg sulfur dioxide using a long-stem funnel with the tip kept well immersed in the solution to prevent the loss of SO₂. This was followed by the addition of 2 mL 0.01% thymol blue solution. Absorbance of the solutions was measured at 545 nm after a reaction time of 5 min and dilution of the solutions to volume with water.

(b) *Extraction procedure.*—To a series of 25 mL standard flasks containing 5 mL 5·10⁻⁵ M ICl in 4.5N H₂SO₄ was added 10 mL trapping solution containing 0–5 mg sulfur dioxide using a long stem funnel with the tip kept well immersed in the solution to prevent the loss of SO₂. This was followed by the addition of 2 mL 0.0016% thymol blue solution. The solutions were diluted to volume with water after a reaction time of 5 min. Then the solutions were transferred to 60 mL separatory funnels and extracted with 5 mL isoamyl alcohol. Absorbance of the organic layer was measured at 550 nm versus reagent blank that had been extracted with 5 mL isoamyl alcohol.

**Results and Discussion**

Iodination of dyes has been used for the determination of sulfur dioxide; SO₂ reacts with iodate in a chloride-containing acid medium to form ICl, which is used to iodinate 2',7'-dichlorofluorescein (10). The method, which involves extraction, followed by selective ionization of the formed product, suffers from poor sensitivity (ε = 4.6 × 10³ L/mol·cm).

In the present method, the absorbance of the uniodinated thymol blue is measured because it provides better sensitivity. In the developed method, a known excess of ICl is used to oxidize SO₂. The unreacted ICl is used to iodinate thymol blue. The decrease in ICl concentration is a measure of the SO₂ concentration. Thymol blue under acidic conditions has maximum absorbance at 545 nm. On treatment with ICl, thymol blue undergoes iodination. The iodinated product has λ_max at 430 nm, and its formation results in a corresponding decrease in absorbance at 545 nm for thymol blue (Figure 1).

When thymol blue is iodinated completely with ICl, the absorbance at 545 nm decreases and reaches a minimum value. With an increase in SO₂ concentration, there is a corresponding decrease in ICl concentration, and as a result, less iodinated thymol blue is formed. In other words, the variation in the concentration of uniodinated thymol blue in the reaction mixture is a measure of the SO₂ concentration (Figure 2).

The absorbance of uniodinated thymol blue was measured at 545 and 550 nm in aqueous and organic solvents, respectively. A linear increase in absorbance with increasing SO₂ concentration was observed.

Various experimental parameters such as acidity, concentration of ICl, and concentration of thymol blue were optimized, and the optimum conditions were incorporated in the recommended procedure. The acidity of the ICl solution can

**Table 1. Extractability of the dye in various solvents**

<table>
<thead>
<tr>
<th>Solventa</th>
<th>Blank (measured against solvent)</th>
<th>4 µg SO₂ (measured against blank)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Toluene</td>
<td>0.002</td>
<td>0.014</td>
</tr>
<tr>
<td>Chloroform</td>
<td>0.002</td>
<td>0.018</td>
</tr>
<tr>
<td>Isobutyl alcohol</td>
<td>0.04</td>
<td>0.485</td>
</tr>
<tr>
<td>n-Butanol</td>
<td>0.038</td>
<td>0.48</td>
</tr>
<tr>
<td>Isoamyl alcohol</td>
<td>0.034</td>
<td>0.52</td>
</tr>
<tr>
<td>Methyl isobutyl ketoneb</td>
<td>0.046</td>
<td>0.455</td>
</tr>
<tr>
<td>Amyl acetateb</td>
<td>0.05</td>
<td>0.45</td>
</tr>
</tbody>
</table>

a The solubilities of various solvents were taken into account, and overall volume was maintained as 5 mL after extraction.
b Extracted in 3.5 mL solvent and diluted to 5 mL with methanolic sulfuric acid.

**Table 2. Determination of sulfur dioxide in a laboratory fume hood**

<table>
<thead>
<tr>
<th>Trapping solution</th>
<th>Sampling rate, L/mina</th>
<th>Amount of SO₂, µgb</th>
<th>Concentration of SO₂, µgc</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>Standard method</td>
<td>Proposed method</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>Standard method</td>
</tr>
<tr>
<td>1.5% Triethanolamine</td>
<td>1.0</td>
<td>8.08</td>
<td>8.25</td>
</tr>
<tr>
<td>Citrate–NaOH</td>
<td>0.4</td>
<td>12.00</td>
<td>11.70</td>
</tr>
<tr>
<td>Buffered formaldehyde</td>
<td>0.5</td>
<td>10.62</td>
<td>10.50</td>
</tr>
<tr>
<td>Glycerol–NaOH</td>
<td>0.4</td>
<td>12.69</td>
<td>12.60</td>
</tr>
</tbody>
</table>

a Sampled on different days; volume of air sampled was 40 L.
b Corresponds to amount of SO₂ present in 10 mL.
c SO₂ (ppb) = SO₂ in 25 mL (µg) x 382/V, where V is the volume of air sampled in liters and 382 is the conversion factor (13) to convert µg/L to ppb SO₂ at 298°K and 101.3 kPa.
vary from 3N to 6N in H₂SO₄, and an acidity of 4.5N H₂SO₄ was maintained during the reaction. The concentration of thymol blue required to produce an absorbance of 0.65 at λ_max was selected, and the corresponding ICl concentration required to decrease the absorbance to 0.05 was fixed.

In the extraction procedure, various solvents (Table 1) were used to extract both iodinated and uniodinated thymol blue (Figure 1); isoamyl alcohol was found to be the best and was selected for the extraction. A shift in λ_max of 5 nm was observed with isoamyl alcohol, as compared with the aqueous solution.

The compatibility of the proposed method with several known trapping solutions for SO₂ was studied. It was observed that trapping solutions like triethanolamine (11), buffered formaldehyde (10), citrate–NaOH (4), and glycerol–NaOH (12) were compatible, whereas tetrachloromercurate (7) was incompatible with the proposed method. In the case of [HgCl₄]²⁻ lower sensitivity was observed because the I₂ formed by the reaction of SO₂ with ICl is also capable of iodinating thymol blue. Because the method is based on the determination of uniodinated thymol blue, a decrease in sensitivity was observed.

**Interference Studies**

The effect of common air pollutants such as H₂S, NO₂, and HCHO on the determination of 24 μg SO₂ was studied by introducing the species directly or in the form of its respective anions along with SO₂. NO₂ did not interfere up to the 30 μg level. At higher levels a decrease in absorbance was noted; however, interference up to the 150 μg level was overcome by the addition of 1 mL 0.5% sulphamic acid to the sample before analysis. Formaldehyde did not interfere up to 5 μg. At higher levels a decrease in absorbance was observed; however, interference up to 1000 μg was overcome by the addition of 1 mL 4.5N NaOH to the sample solution to break the bisulfite adduct before analysis (10). The system could tolerate only 0.5 μg H₂S; at higher levels an increase in absorbance was observed. The interference up to 5 μg H₂S was overcome by oxidizing H₂S with sodium nitrite after fixing SO₂ as the bisulfite adduct by the addition of 1000 μg HCHO. Unreacted nitrite was destroyed by the addition of 1 mL 0.5% sulphamic acid, and the fixed SO₂ was released from the bisulfite adduct by the addition of 1 mL 4.5N NaOH to the sample solution before color development.

**Application**

The proposed method was used for the determination of SO₂ levels in a laboratory fume hood, where sulfurous acid was prepared for the gravimetric estimation of Cu(II) as CuSCN (Table 2), and in the vicinity of furnaces operating with furnace oil or coal (Table 3) as fuel. The air was sampled in 10 mL of different trapping solutions, at the recommended sampling rate, and diluted to 25 mL with the respective trapping solution. Suitable aliquots of the solution were taken and analyzed by the proposed method and the West and Gaeke method. In the West and Gaeke method, the sampled SO₂ in the presence of formaldehyde forms the bisulfite adduct. The bisulfite adduct is used to restore the color of acid-bleached pararosaniline, and the absorbance is measured at 560 nm after a reaction period of 15 min. The results obtained with the 2 methods were comparable.

**Conclusions**

The proposed method is simple, sensitive, and compatible with several trapping solutions for SO₂. The reliability of the proposed method was established by comparing it with the West and Gaeke method. In terms of sensitivity, the aqueous procedures compare well with the West and Gaeke method (ε = 3.2 × 10⁴), whereas the extraction procedure is more sen-

Table 3. Determination of sulfur dioxide in the vicinity of oil-/coal-fired furnaces

<table>
<thead>
<tr>
<th>Fuel</th>
<th>Trapping solution</th>
<th>Sampling rate, L/min</th>
<th>Amount of SO₂, μg</th>
<th>Concentration of SO₂, ppb</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td></td>
<td>Standard method</td>
<td>Proposed method</td>
</tr>
<tr>
<td>Oil</td>
<td>1.5% Triethanolamine</td>
<td>1.0</td>
<td>3.78</td>
<td>1.85</td>
</tr>
<tr>
<td></td>
<td>Citrate–NaOH</td>
<td>0.4</td>
<td>4.06</td>
<td>1.99</td>
</tr>
<tr>
<td></td>
<td>Buffered formaldehyde</td>
<td>0.5</td>
<td>3.69</td>
<td>1.86</td>
</tr>
<tr>
<td></td>
<td>Glycerol–NaOH</td>
<td>0.4</td>
<td>3.87</td>
<td>1.95</td>
</tr>
<tr>
<td>Coal</td>
<td>1.5% Triethanolamine</td>
<td>1.0</td>
<td>4.62</td>
<td>2.35</td>
</tr>
<tr>
<td></td>
<td>Citrate–NaOH</td>
<td>0.4</td>
<td>3.51</td>
<td>1.81</td>
</tr>
<tr>
<td></td>
<td>Buffered formaldehyde</td>
<td>0.5</td>
<td>4.25</td>
<td>2.18</td>
</tr>
<tr>
<td></td>
<td>Glycerol–NaOH</td>
<td>0.4</td>
<td>3.60</td>
<td>1.84</td>
</tr>
</tbody>
</table>

*Sampled on different days; volume of air sampled was 40 L.
*Corresponds to amount of SO₂ present in 10 mL.
*Corresponds to amount of SO₂ present in 5 mL.
*SO₂ (ppb) = SO₂ in 25 mL (μg) x 382/V, where V is the volume of air sampled in liters and 382 is the conversion factor (13) to convert μg/L to ppb SO₂ AT 298°K and 101.3 kPa.
sitive \( (\varepsilon = 4.16 \times 10^4) \). The proposed method can serve as an alternative method for SO\(_2\) determination.

References