CHAPTER SEVEN

Modified Bodekar Reaction For The Detection Of Sulphur Dioxide In Air And Sulphites In Water And Environmental Samples
A modified Bodekar’s reaction has been proposed for the detection of sulphite ion. The reaction involves formation of brick-red precipitate by reaction between zinc nitroprusside and sulphite ion. In the proposed method the reaction has been modified by adding a cationic surfactant tetradecyl trimethyl ammonium bromide which enhances the intensity of the brick-red colour several times. A spot test has been developed for the detection of sulphite ion. The preparation of test paper, indicator tubes and its application in various samples have been described. The lower limit of detection for sulphite ion is 0.05 ppm with this reagent system which is much better than the other reported methods. Most of the common ions do not interfere. The effect of other cationic, anionic and non-ionic surfactants have also been studied and reported.

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Introduction:

Sulphur dioxide is one of the most widely distributed and important air pollutant. It is a colourless non-inflammable gas with a suffocating odour. It plays an important role in the atmosphere because it is actively involved in physicochemical processes such as the formation of aerosols, clouds and acid precipitation. It is formed when sulphur containing substances such as coal, fuel oil, gasoline are combusted. Roasting of sulphide containing ores and sintering of sulphur containing fine ores also emit sulphur dioxide. Its use and production as a by-product in industry is enormous. The combustion of various sulphur containing fuels, auto exhaust, thermal power plant, steel industry, paper and pulp manufacturing and fertilizer plant are generated the large quantities of sulphur dioxide. (3-5)

It is introduced into the environment via its application as a bleaching agent, preservatives, fungicides, 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). It causes irritation to mucous membrane, upper respiratory tract and bronchii. On inhalation it causes sore throat, chest pain, constriction, burning and tearing of eyes, oedema of paralysis (10 - 11). It forms complexes with Fe (III) and Cu (II) both in solution and solid form which distrutively 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, lung tumors and several types of cancer (13).

Some data given below shows the effect of sulphur dioxide on humans. The data is collected from different sources and are given for healthy human under experimental conditions in the laboratory condition, not comparable to the ambient air where the synergistic effects of other pollutants would probably cause different reactions(14).

**Effect of Sulphur dioxide on humans.**

<table>
<thead>
<tr>
<th>Conc. ppm</th>
<th>Exposure time</th>
<th>Effects</th>
</tr>
</thead>
<tbody>
<tr>
<td>0-0.6</td>
<td>-</td>
<td>No detectable response.</td>
</tr>
<tr>
<td>0.15-0.25</td>
<td>1-4 d</td>
<td>Cardiorespiratory response.</td>
</tr>
<tr>
<td>1.0-2.0</td>
<td>3-10 min</td>
<td>Cardiorespiratory response in healthy subjects.</td>
</tr>
<tr>
<td>1.0-5.0</td>
<td>-</td>
<td>Detectable responses, tightness in chest</td>
</tr>
<tr>
<td>5.0</td>
<td>1h</td>
<td>Choking and increased lung resistance to air flow.</td>
</tr>
<tr>
<td>10.0</td>
<td>1h</td>
<td>Severe distress, some nose bleeding</td>
</tr>
<tr>
<td>Greater than 20</td>
<td>-</td>
<td>Digestive tract affected, eye irritation also.</td>
</tr>
<tr>
<td>400-500</td>
<td>-</td>
<td>Dangerous for short period of time.</td>
</tr>
</tbody>
</table>
Concentration as low as 1-2 ppm may lead in a few hours to acute damage in the form of localized destruction of leaf tissue. In sensitive plants chronic damage may also occur at 0.3 ppm sulphur dioxide or higher. Highly acidic rainfall and elevated levels of atmospheric sulphur dioxide severely damage crops, forests and building materials (15-16). It increases the soil acidity making it unstable for plant growth. Cytogenic effect of sulphur dioxide on cytotypes of Solanum nigrum complex has been reported recently (17).

USEPA has recommended maximum allowable limit of 0.03 ppm for daily exposure for 1 h duration (18). 5 ppm is the permissible exposure limit value for 8 hrs duration (19).

Sulphites when present in water causes anxiety, nausea, eye strain, asthma etc. (20). It reduces the dissolved oxygen content and chemical oxygen demand of water which is harmful for aquatic species.

Because of its importance, wide occurrence, and toxicity on all living beings, suitable and sensitive analytical methods are required (21) for its detection and determination in the environmental samples. Several analytical methods such as atomic absorption spectrometry (22), GC-MS (23), FT-IR (24), gold film sensor (25), GC (26-27), FIA (28-30), HPLC (31), fluorescence photometric (32), UV spectrometry (33) and a large number of spectrophotometric methods (34-39) are available in literature. Various field methods for rapid detection or measurements are also available in literature (40-44). Bodekar's reaction has been used in the preparation of test paper for the detection of sulphur dioxide (41). It has been reported that addition of a base increases the intensity of colour reaction. In search of better reagent to increase the intensity of colour reaction and detection limit many reagents such as zinc-nitroprusside-pyridine (40), zinc nitroprusside-sulphite ion (41), a-α bipyridyl or 1:10 phenanthroline (42), malonyldihydrazide (43), oxalyldihydrazide (44) have been reported.

In recent years, it has been reported that the different surfactants show catalytic or inhibition effect on the sensitivity of the colour reactions (45-46). Hence various surfactants have been studied here to find out whether they have the property to enhance the sensitivity of Bodekar reaction. In the present communication tetradecyl trimethyl ammonium bromide was found to be the most suitable surfactant to enhance the intensity of the brick-red precipitate formed in a Bodekar's reaction. The reaction is favourably utilized in the preparation of test papers and indicator tubes for the detection of sulphur dioxide in air and sulphite in water and food samples.

Experimental:

**Apparatus** - Fritted midget impingers of 35 ml capacity was used for air sampling. PIMCO make calibrated rotameter was used for adjusting the flow rate.
Reagents: All chemicals used were of AnalaR grade and double distilled water was used throughout the experiment.

**Zinc acetate** - 1 M zinc acetate dihydrate in 5% (v/v) glycerol.

**Sodium nitroprusside** - 2% (m/v) aqueous solution.

**Tetradecyl trimethyl ammonium bromide (TTAB, Sigma 99%)** - 1% aqueous solution.

**Standard sulphite solution** - Sulphite solution containing 0.32 - 0.40 mg ml⁻¹ of sulphur dioxide was prepared by dissolving 0.2 gm of pre-dried sodium sulphite ion in 250 ml distilled water. Sulphite solution was standardised iodometrically. Working standard was prepared by appropriate dilution.

For air analysis, sulphur dioxide was produced from freshly prepared sodium sulphite and 2 ml of 0.5 M hydrochloric acid mixture which was absorbed in the indicator tube using an air sampling train, consisting of rotameter, vacuum pump, standard 35 ml impingers and traps.

**Preparation of test papers and indicator tubes** -

**Test paper** - Test papers were prepared by cutting Whatman filter paper no. 1 into strips of size 5 x 2 cm and dried in reagents zinc acetate, sodium nitroprusside and tetradecyl trimethyl ammonium bromide (TTAB) serially. The filter papers were dried after each dip in a snap action thermostat maintained at ~ 40°C for 30 min. The light cream coloured test papers were stable for one week when kept in tightly closed brown bottles.

**Indicator tube** - Well cleaned and dried tubes were taken. The reagent solution was added to the silica gel kept in a watch glass in a snap action thermostat maintained at ~ 40°C for 20 mins. Then the silica gel was used and filled to 2 cm length in indicator tube and its ends were sealed with wads of glass wool about 1 cm in length. Then the sealed tubes were kept in desicator. These tubes were stable for one month.

**Detection of Sulphur dioxide in Air** -

**Procedure with test paper and indicator tubes** - Test papers were moistened with humectant glycerol 5% (v/v) and inserted in a test paper holder which was connected through a rotameter. The air was drawn through the test paper at a rate of 0.50 l min⁻¹. The test paper turned brick-red in presence of sulphur dioxide in the sample.

Sulphur dioxide was also detected with the above reagents in solution. Samples of sulphur dioxide were drawn through 5 ml of zinc acetate solution taken in 35 ml impinger. After sampling, 0.5 ml of sodium nitroprusside and 1 ml of TTAB were added serially to the impingers. Initially a red colouration was formed which gradually converted to bulky brick-red precipitate which settled down within few minutes.

**Indicator tube** - For the estimation of sulphur dioxide the sealed ends of the indicator tubes were cut and one end of the tube was connected to the source of suction. The flow rate
was controlled with a PIMCO make calibrated rotameter. The flow rate was maintained at 0.50 l min⁻¹ for ~ 20 min. Indicator tubes stained brick-red in the presence of sulphur dioxide which was estimated by comparing the colour obtained with that of the standard treated similarly.

Detection and Semiquantitative Determination of Sulphur Dioxide in Air and Sulphite in Water and Environmental Samples.

In the laboratory ~ 100 mg sulphur powder was burnt and the air was drawn through the test paper at a rate of 0.75 l min⁻¹ with the help of a suction pump. The test paper turned brick red which indicates the presence of sulphur dioxide in work-room air.

For the detection of sulphite in water 1 ml each of the zinc acetate, sodium nitroprusside and TTAB were taken in a 10 ml beaker serially. A cream coloured solution was formed. The solution was taken in a spot plate. To this spot plate, one drop of sulphite solution (containing 1 μg SO₂ in 1 ml) was added. Immediately a brick-red precipitate was formed which indicated the presence of sulphur dioxide in sample.

The proposed method was satisfactorily applied for the detection of sulphites in soft drinks (where sulphites are normally added as preservatives), mashed potatoes, grapes juice and dried apple and the results found are shown in Table 1.

Results and Discussion:

Proposed method is simple, sensitive and rapid for the detection of sulphur dioxide. The colour produced in the proposed method was much more intense and sensitive than method using oxalyl dihydrazide (ODH, detection limit 0.2 ppm). By this method as low as 0.1 ppm of sulphur dioxide present in air or 0.05 ppm sulphite present in water can be easily detected whereas other methods have lower sensitivity.

The brick-red precipitate was not stable in organic solvents like chloroform, carbon tetrachloride, benzene, methanol, ethanol, glycerol etc. Either the precipitate decomposed or remained undissolved in these solvents.

The pH of the coloured solution after the formation of precipitate was found to be in the range of 5.5 - 5.8. The reaction is highly sensitive to pH as addition of a small amount of acid or alkali decomposed the precipitate and discharged the colour.

To assess the validity of the method effect of foreign species on the reaction have been studied. Nitrite, nitrate, carbonate, sulphate, phosphate, formaldehyde, chloride, ammonia etc. present in water and nitrogen dioxide, carbon dioxide, carbon monoxide etc. present in air did not interfere with the colour reaction. Sulphide ion gave similar colour reaction. However its interference can be eliminated by passing the gas samples through mercury (II) chloride solution (40).
The effect of other cationic, anionic and non-ionic surfactants was studied to find out the best surfactant for the reaction and it was found that the anionic and non-ionic surfactants have no effect on the intensity of color.

Increase in the intensity of color by addition of TTAB was supposed to be due to formation of $[\text{Zn(TTAB)}_n]_z$, $\text{Fe(CN)}_3\text{NO.SO}_3^-$. The interaction of nitroprusside and sulphite ions in aqueous solution gives the red, highly dissolved sulphito nitroprusside ions, $\text{Fe(CN)}_3\text{NO.SO}_3^-$. The addition of zinc ions results in the formation of sparingly soluble zinc sulphito nitroprusside and then sensitivity of the reaction increased markedly.

It is also found that the amount of sulphito nitroprusside ion formed in solution is increased not only by the addition of zinc ions but also by the addition of alkali metal ions. The effect of alkali metal ions appears to be due to the formation of ion pairs of the type $\text{Fe(CN)}_3\text{NO.SO}_3^\text{M}^+\text{ where M is the alkali metal. The effect is more pronounced with the larger alkali metal ion.}$

The sensitivity of the reaction involving zinc ion has been shown to be further improved by the addition of $\alpha,\alpha\text{-Bipyridyl, MDH, ODH (42-44)}$. The surfactant TTAB was added to the colour reaction to increase the solubility of the complex but it has been found that it enhances the sensitivity of the reaction. This is believed to be due to the low solubility of $[\text{Zn(TTAB)}_n]_z\text{Fe(CN)}_3\text{NO.SO}_3^-$ complex.

**Application:**

Sulphur dioxide and sulphites have been reported to be present in beer, wine, grape juice, dried apple, mashed potatoes etc. (47-50). The proposed method was satisfactorily applied for the detection and semiquantitative determination of sulphur dioxide in work-room air and sulphites in water and environmental samples. The results obtained were in good agreement with those obtained by reported method (44). Table 1. The semiquantitative determination in environmental samples was done by comparing the colour intensities obtained by varying amounts of sulphites (0.05 - 3 ppm).

**Conclusion:**

The proposed method is rapid, simple, selective and sensitive. Table 2. Reagents used were easily available and the test papers, indicator tubes can be prepared easily. The proposed method can be applied for field detection of sulphur dioxide and sulphites and without any special modification up to 0.05 ppm of sulphite can be easily detected by this method.
Table - 1. Application of the method in environmental samples.

(Flow rate : 0.75 l min⁻¹)

<table>
<thead>
<tr>
<th>Sample</th>
<th>Sulphur dioxide found, ppm*</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>P</td>
</tr>
<tr>
<td>Work-room air</td>
<td>0.60 (±0.020)</td>
</tr>
<tr>
<td>Beer**</td>
<td>0.50 (±0.010)</td>
</tr>
<tr>
<td>Cola soft drink**</td>
<td>2.50 (±0.000)</td>
</tr>
<tr>
<td>Orange squash**</td>
<td>1.25 (±0.000)</td>
</tr>
<tr>
<td>Mashed potatoes***</td>
<td>0.85 (±0.015)</td>
</tr>
<tr>
<td>Dried apple***</td>
<td>0.80 (±0.010)</td>
</tr>
</tbody>
</table>

* Mean of the three replicate analysis.

a = 100 mg of sulphur powder was burnt.

** Amount of sample = 25 ml.

P = Proposed method, R = Reported method.

*** Amount of sample = 15 gm.

Table - 2. Comparison with other detection method.

<table>
<thead>
<tr>
<th>Reagent/Ref.</th>
<th>Detection limit, ppm</th>
<th>Remarks</th>
</tr>
</thead>
<tbody>
<tr>
<td>Zinc nitroprusside-sulphite ion⁴¹</td>
<td>3.5</td>
<td>Less sensitive.</td>
</tr>
<tr>
<td>Zinc nitroprusside-pyridine⁴⁰</td>
<td>5.0</td>
<td>Less sensitive.</td>
</tr>
<tr>
<td>α-α Bipyridyl or 1:10 Phenanthroline⁴²</td>
<td>0.5</td>
<td>Less sensitive.</td>
</tr>
<tr>
<td>Malonyldihydrazide⁴³</td>
<td>0.2</td>
<td>Less sensitive.</td>
</tr>
<tr>
<td>Oxalyldihydrazide⁴⁴</td>
<td>0.2</td>
<td>Less sensitive.</td>
</tr>
<tr>
<td>Tetradecyl trimethyl ammonium bromide (TTAB, Proposed method)</td>
<td>0.1</td>
<td>More sensitive.</td>
</tr>
</tbody>
</table>
References:

28 Gu X.; Wei W.; Nei L. and Yao S., Analyst, 1998, 123(2), 221.