

Analytical, Nutritional and Clinical Methods

An optoelectronic instrument for the determination of sulphite in beverages

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Abstract

The paper describes an optoelectronic device that has been designed and developed to measure the sulphite concentration in beverages for quality evaluation. A selective and sensitive method for determination of sulphite is based on the reaction with pararosaniline acid bleached dye and formaldehyde solution, which gives violet colored complex having absorption maxima at 560 nm. Lambert–Beer's law is obeyed in the concentration range up to 25 µg/ml (25 ppm) of test solution within an accuracy of $\pm 0.05 \mu\text{g/ml}$ (0.05 ppm). The instrument involves the use of high intensity green light emitting diode (LED) of wavelength 565 nm as light source. BPW21 photodiode having the relative spectral sensitivity above 90% in the range of 500–600 nm has been used as a detector, for the determination of sulphite concentration.

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1. Introduction

Sulphite is widely used as an additive in food and beverages to prevent oxidation, bacterial growth and to control enzymatic reactions during production and storage. Sulphite poses a greater danger when consumed above permissible limit (set by the US Food and Drug Administration) by causing nasal congestion, coughing, breathing difficulties, asthma, itching, hives and other skin rashes. Sulphite also causes headache, abdominal pain, diarrhea resulting in fatigue and irritation. The above symptoms occur quickly within 20–30 min after consuming sulphite added products such as bottled canned or frozen fruits, baked foods, beer and wine etc. Sulphite has been determined by numerous methods such as titrimetric method in which sulph-

ite is converted into sulphur dioxide and further oxidized to sulphuric acid using hydrogen peroxide and subsequently titrating against alkali (William, 1984). Ion chromatography with conductivity detector has been used for sulphite determination in food (Anderson, Warner, Daniel, & Padgett, 1986; Sullivan & Smith, 1985). Sulphite contents of some foods and beverages by capillary electrophoresis have earlier been reported (Sadecka & Polonsky, 1999; Walker, Zaugg, & Walker, 1997; Trenerry, 1996). A flow injection gas phase molecular absorption spectroscopic method for the determination of sulphite in aqueous solution has also been used (Safavi & Haghghi, 1997). An analytical pervaporation technique has been reported for online determination of total sulphur dioxide in wines (Mataix & Luque de Castro, 1998) in order to remove sulphur dioxide from the matrix. An overview of application of analytical pervaporation in food analysis for sulphite and sulphur dioxide was explained (Amador-Hernandez & Luque de Castro, 2000).

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Fig. 1. Optoelectronic instrument for the determination of sulphite.

In the present work a portable battery operated, light weight (2.5 kg) dedicated optoelectronic instrument (Fig. 1) has been developed using an LED of 565 nm as light source and BPW21 as a photo-detector for the determination of sulphite concentration. Sulphite reacts with pararosaniline acid bleached dye and formaldehyde solution to form a violet colored complex (Fig. 2) (Pate, Ammons, Swanson, & Lodge, 1965). The detector has peak spectral response at 565 nm where LED operates. The system directly displays the concentration of sulphite in ppm ($\mu\text{g/ml}$) on liquid crystal display (LCD). The zero value on the display can be adjusted with a reagent

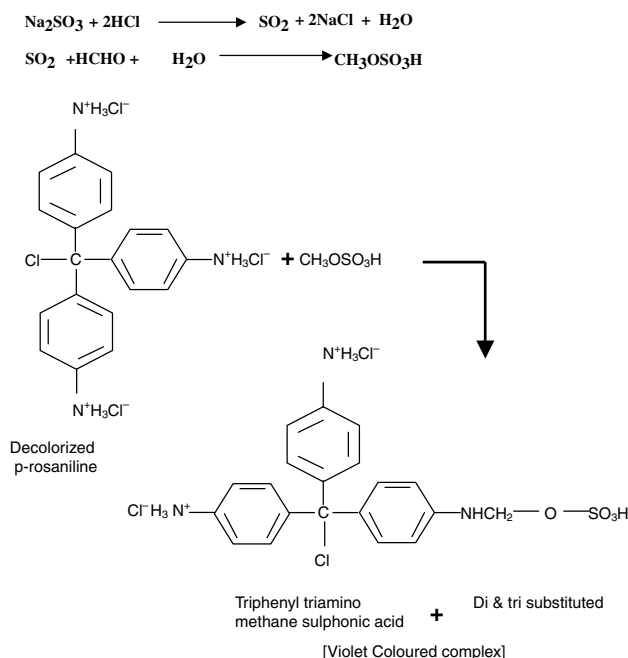


Fig. 2. Reactions scheme of violet colored complex solution.

blank and no further calibration is needed for concentration measurements.

2. Materials and methods

2.1. Instrumentation block schematic

The system consists of LED as light source, cuvette holder, photodetector, current to voltage ($I-V$) converter, Logarithmic amplifier and LCD having display range up to second place of decimal (3&1/2 digit digital panel meter) as shown in Fig. 3. Dual power supply (rechargeable battery) of $\pm 6\text{ V}$, 4.5 AH has been used for the operation of the system. The power supply has been designed to get constant voltage, which makes the system free from voltage fluctuations.

The existing spectrophotometers usually have tungsten or tungsten halogen lamp as a light source, optical filter or grating, detector and display system. Light source used in the present system is a high intensity green LED (wavelength 565 nm) with specifications: $I_f = 30\text{ mA}$, $V_f = 2.2\text{ V}$, operating temperature range = -20 to $100\text{ }^\circ\text{C}$. The light source has been selected keeping in mind the complementary colour of the test solution. Use of LED as light source reduces the size of the system as no further filter or grating or focusing optics is required. A constant DC power supply reduces the noise from the light source to a minimum level.

The sample or reference compartment is light proof and constitutes a kinematically engineered cell holding device to ensure reproducible placement of the sample/reference cell in the path of light beam. LED is fitted at one side of the cell compartment for the light beam to traverse through the cuvette holder. The detector is attached to the other side of the cell holder. The detector

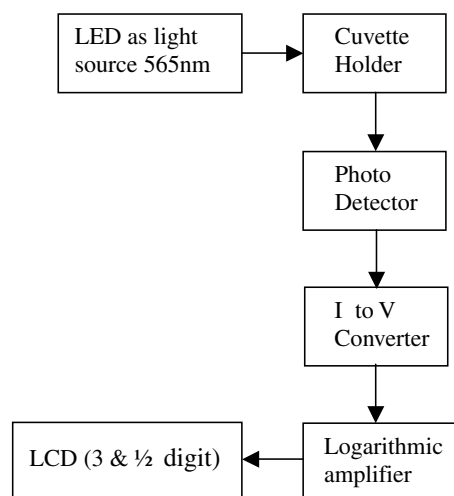


Fig. 3. Block diagram of the optoelectronic system.

and the LED are at right angles to the incident and exiting light. It is designed such that the reflective light losses do not occur. The sample holder can accommodate a cuvette of 1 cm internal diameter and 6 ml capacity. A visible range photo-detector (RS catalogue, 2003–2004, RS Components and Controls (India) Ltd., An Indo-British joint venture between RS Components Ltd., of UK and Controls & Switchgear Co. Ltd. of India, New Delhi) is selected for wavelength range: 460–750 nm; power dissipation: 250 mW (max). It is ideal for low light level applications where a very high signal to noise ratio is important. The relative spectral sensitivity of BPW21 is between 0.9 to 1.0 at a wavelength from 500 to 600 nm. TL 441 has been used as logarithmic amplifier (Texas instruments manual, 2000), which contains four 30 dB logarithmic stages. Gain in each stage is such that the output of each stage is proportional to the logarithmic of the input voltage over the 30 dB input voltage range. The absorbance output of log amplifier is in millivolts, which has been calibrated in parts per million ppm ($\mu\text{g}/\text{ml}$) and is directly displayed on LCD.

2.2. Materials

Sodium sulphite, MERCK Germany guaranteed reagent (GR), formaldehyde (GR) 40% MERCK India, hydrochloric acid (GR) MERCK India, pararosaniline hydrochloride microscopic stain (MS) s.d Fine-Chem Limited India. All the chemicals were used without further purification.

2.3. Samples

Different types of beverages, which include Indian wine, Indian whisky and Indian cold drinks were collected from the reputed stores. These samples collected were in sealed packages from their fresh stocks. These samples, with batch numbers marked on them were used prior to their expiry date.

2.4. Preparation of standards, samples and reagents

Sodium sulphite solution (25 $\mu\text{g}/10$ ml of SO_2). Dissolved 0.200 g anhydrous sodium sulphite in double distilled water and made the volume up to 100 ml in a volumetric flask. Diluted the solution further to get 25 $\mu\text{g}/10$ ml of sulphur dioxide. Fresh solutions were prepared to check random calibration, as sodium sulphite is not stable on its long storage.

Pararosaniline hydrochloride dye solution. Forty milligram of pararosaniline hydrochloride dye was dissolved in 40 ml of distilled water. To it added 6 ml of concentrated HCl and the volume was made to 100 ml in a volumetric flask.

Formaldehyde solution (0.2%). 0.5 ml of formaldehyde (40%) was added to a 100 ml volumetric flask

and diluted the solution with distilled water to make the volume up to the mark.

2.5. Calibration procedure

In a series of graduated glass stoppered cuvettes, 1, 2, 3, 4, 5, 6, . . . , 10 ml of 25 $\mu\text{g}/10$ ml solution were taken. Required volume of distilled water was added water to each solution to make their volume 10 ml. followed by the addition of 1 ml of pararosaniline dye solution to each cuvette. Mixed the contents well and then added 1 ml of formaldehyde solution. Kept the solutions for 20 min for the full color development.

2.6. Preparation of reagent blank

To 10 ml distilled water added 1 ml of pararosaniline dye solution. Mixed well and added 1 ml of formaldehyde solution and kept the solution for 20 min.

2.7. Calibration curve

Absorbance value of each solution was measured against the reagent blank, at 560 nm using a quartz cell of 1 cm path length with Perkin–Elmer (Lambda-35) UV–Visible spectrophotometer. A calibration graph was plotted for concentration of sulphite against measured absorbance, which is linear in the sulphite concentration range up to 25 $\mu\text{g}/\text{ml}$ (expressed as SO_2).

2.8. Calibration of the instrument

The reagent blank and a series of standard sulphite solutions in the concentration range 0–25 $\mu\text{g}/\text{ml}$ (in 10 ml solution) were prepared as per calibration procedure. The instrument was set to zero with the reagent blank. The calibration of the instrument was made using three standard sulphite solutions of 5, 10, 20 $\mu\text{g}/\text{ml}$ adjusting the concentration display with the potential POT provided on the front panel of the instrument. All the standards were checked with the Perkin Elmer (Lambda-35) spectrophotometer in the concentration mode.

2.9. Testing procedure of beverage samples

Pipetted 1 ml of each beverage sample and diluted to 10 ml with distilled water. To it added 1 ml of pararosaniline dye solution and 1 ml of formaldehyde solution. Kept the solution for 20 min for the colour development. The instrument was set to zero with reagent blank. The cuvette with test solution was inserted in the sample holder and the concentration was measured. Each beverage sample was analyzed at least five times at 24 h interval. For beverages having sulphite concentration more than 25 $\mu\text{g}/\text{ml}$, further appropriate dilution was carried out.

3. Results and discussion

The optoelectronic system was first validated with standard solutions of varying concentration to determine its linearity range. Each standard solution was analyzed five times to check reproducibility of the instrument. The detector response for sulphite contents in beverages was found to be linear up to 25 µg/ml in 10 ml solution. The observed concentration values, using optoelectronic system, for different standard samples in the concentration range up to 25 µg/ml in 10 ml solution, at 2.5 µg/ml interval are given in Table 1. Reproducibility of results over the studied concentration range was satisfactory for all test solutions (standard concentration 5 µg/ml: deviation ±1.2%; standard concentration 10 µg/ml: deviation ± 1.2%; standard concentration 15 µg/ml: ±1.4%, standard concentration 20 µg/ml: deviation ± 1.5% and standard concentration 25 µg/ml: deviation ± 2.0%).

The sulphite contents of a number of beverages (wine, whisky and soft drinks) were determined with the developed optoelectronic instrument. The results were compared with those obtained using standard titration

method. The total sulphite contents in white and red wines are found to be more than 50 µg/ml. In order to perform the sulphite analysis with the optoelectronic system in the optimum concentration range, as per the detector response up to 25 µg/ml in 10 ml solution, the wine samples were further diluted with distilled water, by a factor of 5–10. The sulphite contents were calculated from the mean of five replica of the same beverage. Relative standard deviations of the displayed values of sulphite contents for the wine beverages are within 0.6–1.5%. The results of the measurements using optoelectronic system as well from titrimetric analysis after blank correction given in Table 2. It can be seen that the results that both methods are in fair agreement. The effect of dilution of the wine on the total sulphite contents measurement is insignificant with the present optoelectronic instrument. The relative standard deviation in concentration observed from the optoelectronic instrument, in the five brands of whiskey varies from 0.5% to 1.5%. In these samples no further dilution was carried out, as their sulphite contents lie within the calibration range of the optoelectronic instrument. The results when compared with the titrimetric method, gave a close agreement (Table 2). Since the sulphite contents in most of the whisky beverages are low (<5 µg/ml), for a better accuracy an aliquot 100 ml of its sample was taken for titrimetric analysis. The accuracy of the optoelectronic was investigated by adding a known amount of sulphite standard to five samples of whisky. The results of these measurements are comparable with the known values.

Study on the interference of nitrite in the determination of sulphite contents using optoelectronic system was also carried out. On adding nitrite up to 1 µg/ml to a sample solution, no change was observed in the sulphite concentration. Tolerable nitrite concentration in drinks being 0.1 µg/ml. The use of LED has not only minimized the size of the instrument but has also

Table 1

Comparison of results of standard samples with the optoelectronic instrument

Sr. no.	Standard sample (µg/ml)	Values displayed on the instrument (µg/ml)
1.	2.50	2.45
2.	5.00	4.92
3.	7.50	7.51
4.	10.00	9.80
5.	12.50	12.57
6.	15.00	14.87
7.	17.50	17.32
8.	20.00	19.98
9.	22.50	22.30
10.	25.00	24.70

Table 2

Comparison of the levels of sulphite (µg/ml) determined using optoelectronic instrument and usual titrimetric method for a variety of beverages

Type of Indian beverage	Standard titration method after blank correction		Optoelectronic system against reagent blank	
	Total SO ₂ (µg/ml)		SO ₂ (µg/ml)	Dilution factor
<i>Riviera wine</i>				
White Brand-I	57.6		55.0 ± 0.8	10
Red Brand-II	67.7		64.5 ± 0.8	10
<i>Grover wine</i>				
White Brand-I	125.6		124.0 ± 1.0	10
Red Brand-II	135.0		128.0 ± 1.2	10
Director's Special Whisky	4.7		4.92 ± 0.06	–
Bagpiper Whisky	3.8		3.54 ± 0.04	–
Signature McDowell	3.5		3.25 ± 0.05	–
Red Knight Whisky	4.0		3.70 ± 0.02	–
Gin 'n' Lion	4.8		5.00 ± 0.04	–
Gulab Desi	2.4		2.00 ± 0.03	–
Pepsi Soft drink	–		–	–

dispensed with the need of the usual accessories such as lamp, grating and lens. Further, since no calibration is required in the routine analysis, this makes the present system more handy and dedicated.

4. Conclusion

A portable optoelectronic system has been designed and developed using 565 nm LED. The system is compact and provides efficient, reproducible and precise measurements of sulphite contents in liquid sample, such as beverages, for their quality evaluation. The selective and sensitive method involves for the determination of sulphite, is based on the reaction between pararosaniline acid-bleached dye and formaldehyde solutions, which gives violet colored complex having absorption maxima at 560 nm. Lambert–Beer's Law is obeyed in the concentration range up to 25 µg/10 ml of test solution within an accuracy of ±0.05 µg/ml. The instrument involves the use of high intensity green light emitting diode (LED) of wavelength 565 nm as the light source. BPW21 photodiode, having the relative spectral sensitivity above 90% in the range of 500 – 600 nm has been used as detector, for the measurement of sulphite concentration.

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