

Single-Drop and Nanogram Level Determination of Sulfite (SO₃²⁻) in Alcoholic and Nonalcoholic Beverage Samples Based on Diffuse Reflectance Fourier Transform Infrared Spectroscopic (DRS-FTIR) Analysis on KBr Matrix

SANTOSH K. VERMA AND MANAS K. DEB*

School of Studies in Chemistry, Pt. Ravishankar Shukla University, Raipur 492 010, Chhattisgarh, India

The diffuse reflectance Fourier transform spectroscopic (DRS-FTIR) method, using potassium bromide matrix, has been developed for the one-drop microdetermination of sulfite in beverage samples. The present method is very simple, rapid, and precise for the determination of sulfite. The nanogram level of sulfite determination is based on the selection of a quantitative analytical peak at 495 cm⁻¹ among the three observed vibrational peaks obtained by diffuse reflectance Fourier transform infrared spectroscopy (DRS-FTIR). As little as a single drop of sample is sufficient for quantitative analysis of sulfite. The limit of detection (LOD) and the limit of quantification (LOQ) of the method are found to be 8 and 40 ng of SO₃²⁻ 0.1 g⁻¹ of KBr matrix, respectively. The linear range of the method (LR) as well as the LOD based on the concentration of sulfite in the solution are 5–500 and 0.8 μg/mL, respectively. The precision in terms of standard deviation and relative standard deviation value at a level of 100 ng of SO₃²⁻ 0.1 g⁻¹ of KBr for *n* = 10 are found to be 2 ng of SO₃²⁻ and 2.3%, respectively. The relative standard deviation (*n* = 10) for the determination of sulfite in beverage samples available in the local market was observed to be in the range of 2.4–7.8%. The method is free from interionic effects of foreign species. No sample pretreatment is required in this method. The proposed method avoids the requirement of large numbers and bulk amounts of reagents. The method is well-suited to the need of green chemistry.

KEYWORDS: DRS-FTIR; sulfite determination; nanogram level; beverage samples; green chemistry

INTRODUCTION

Sulfites are very essential as a preservative for many foods, beverages, and pharmaceutical products to prevent oxidation and bacterial growth and to control enzymatic reactions during production and storage (1–3). The addition of sulfites to some foods such as beer and wine is permitted in most countries. The use of sulfite serves several purposes simultaneously, both in fermentation and in storage (4). However, nowadays due to the reported harmful effects of sulfite and sulfur dioxide it is considered as a hazard to human health, so the extensive use of sulfite in foodstuffs has come under rigorous control (5). Although numerous useful methods are available to determine sulfite and sulfur dioxide (6–11) in different kinds of samples, these methods are not fully satisfactory. There are many analytical techniques available for the detection of sulfite, including spectrofluorometry (12, 13), spectrophotometry (14–17), gas diffusion flow injection analysis (1, 18–21), phosphorimetry (22), chromatography (23–27), electrochemical methods (28, 29), enzymatic techniques (30, 31), chemiluminescence (CL) measurements (32–37), capillary electrophoresis (38), sulfite biosensors (39–43),

flow injection analysis (44), and ion chromatography with indirect UV detection method (45). However, some of them are not selective or sufficiently sensitive, and some need weighty pretreatment. Invariably, all methods reported above also require more or less a large number of eco-unfriendly chemicals. In recent studies (46, 47), we noticed that diffuse reflectance Fourier transform infrared spectroscopy (DRS-FTIR) could serve as an excellent analytical tool for trace determination of inorganic species in a variety of samples at tremendously low sample size. To date there is no report on qualitative or quantitative determination of sulfite using the DRS-FTIR technique. The present paper describes the development of a new, rapid, and precise analytical method for the determination of sulfite in beverage samples. This method is absolutely free of uses of harmful and massive amounts of reagents and thus strongly supports the present day need of green chemistry, too.

MATERIAL AND METHODS

Chemicals and Reagents. Potassium bromide used in this analysis was of infrared spectrometric grade from Merck KGaA, Darmstadt, Germany. Standard stock solution of sulfite was prepared by dissolving a suitable amount of sodium sulfite (Na₂SO₃), analytical reagent grade,

* Author to whom correspondence should be addressed (e-mail debmanas@yahoo.com; telephone +91 771 2593367).

Table 1. Infrared Absorption Bands and Different Modes of Vibration for Sulfite When Used as Sodium Sulfite

vibrational mode	characteristic absorption peak range found in the present work, cm^{-1}	absorption peak range reported earlier (47–49), cm^{-1}
asymmetric stretching (ν_3)	1280–1145 (blurred, unresolved)	1230–1010
symmetric stretching (ν_1)	1035–870 (very strong and broad)	1090–990
bending vibrations (ν_2)	645–604 (strong and sharp)	660–615
bending vibrations (ν_4)	510–465 ^a (strong and sharp)	525–470

^a Absorption peak range with maxima at 495 cm^{-1} chosen for quantification.

Merck. The stock sulfite solution, due to instability, was preserved in a dark and cool place for a maximum of 48 h or it was prepared when needed. Appropriate dilutions were made to obtain solutions containing sulfite in the concentration range of 50–5000 ng/10 μL . All chemicals, other than potassium bromide, used were of analytical reagent grade (Merck, Poole, Dorset, U.K.).

Apparatus. Diffuse reflectance, model DRS-8000A, Shimadzu Corp. Analytical and Measuring Instruments Division, Kyoto, Japan, and FTIR spectrometer, model 8400S Shimadzu Corp., equipped with an L-alanine doped deuterated triglycine sulfate (DTGS) detector was used for the sample scanning. This equipment is supported with the software Shimadzu IR Solution 1.10 (© 2002 Creon-Laboratory-Control AG Shimadzu). For the weight measurement, a Sartorius electronic balance (Göttingen, Germany; model CP225D) (precision 10 μg) was used. The FTIR was set with the following instrumental specifications: apodization function, Happ-Ganzel; resolution, 2 cm^{-1} ; no. of scans, 45; measurement mode, absorption; beam, internal; mirror speed, 2.8 mm s^{-1} . A variable volume (10–100 μL) micropipet (GlaxoSmithKline Pharmaceuticals Ltd.) was used for handling liquid volumes. Calibrated glass apparatuses were used for volumetric measurements. Because of the high sensitivity of the method, special care was taken during handling of all glassware to avoid contamination. Glassware was cleaned with an ultrasonic bath (Spectralab, Thane, India; model UCB-40) using mild detergent and, after proper washing, rinsed with ultrapure water. A Millipore ultrapurifier system was used to obtain pure distilled water.

Preparation of Calibration Curves for Sulfite Determination. A series of exactly weighed (100 mg) granular KBr were taken in small beakers (5 mL). Into this were poured varied known concentrations of sulfite in the range of 50–5000 ng/10 μL (a single drop volume) with the help of micropipet tips. Then all of the standard KBr matrix was dried in a water bath at a temperature around 40 $^\circ\text{C}$ for 3 min. After drying, KBr matrix was ground to fine particles in an agate mortar for 1–2 min and thoroughly mixed. This dried standard was analyzed by the DRS-FTIR against a blank prepared under similar condition.

Sample Preparation for Sulfite Determination. As such there is no special sample preparation method required in this method. A single drop (10 μL) of the beverage is taken and sprayed over preweighed potassium bromide substrate. After drying over a water bath, this spiked KBr can be directly put in DRS-FTIR, and spectra may be obtained. These spectra can be used for both the qualitative and quantitative analysis of sulfite. However, for total sulfite determination in real acidified samples, alkaline hydrolysis is required for prevention of loss of analyte by volatilization of SO_2 .

RESULTS AND DISCUSSION

Detection of Qualitative Vibrational (Infrared) Peaks for Sulfite. DRS-FTIR provides useful information about the presence of the sulfite. The descriptions on characteristic IR absorption bands for sulfite as found in the literature (47–49) were used for the interpretation of the FTIR spectra of sulfite functional groups in the present work. All of the characteristic IR absorption bands for sulfite are checked by employing standard samples. This paper qualitatively identifies the presence of sulfite species by the study of spectra of its pure salt or compound. The presence of sulfite is commonly reported to be related to strong absorption bands around 1230–1010, 1090–990,

660–615, and 525–470 cm^{-1} . In the present work, the spectral study of the solutions prepared using Na_2SO_3 salt shows four strong (broad and sharp) absorption bands at 1035–870, 645–604, and 510–465 cm^{-1} with their maxima at 973, 633, and 495 cm^{-1} , respectively. The infrared absorption band found in the range of 1280–1145 cm^{-1} is very broad and unresolved and is of no analytical interest. The band at 973 cm^{-1} shows the strongest but broad peak, and the peak observed at 633 cm^{-1} is relatively stronger than the peak at 495 cm^{-1} for sulfite. Two-point baseline corrections were performed between 1100 and 400 cm^{-1} in all cases for the observation of all qualitative spectral peaks due to SO_3^{2-} . **Table 1** shows the FTIR absorption bands for the different modes of vibration of sulfite.

Quantitative and Analytical Infrared Peak Selection for Sulfite Determination. Interestingly, the strongest but broad peak at 973 cm^{-1} disappears at low sulfite level, and also there is the shift in spectral position. Probably on dilution the pyramidal structure with C_{3v} symmetry of sulfite collapses and acquires a planar symmetric structure with D_{3h} symmetry gradually, and thus the symmetric stretch ν_1 becomes infrared inactive. The peak at 633 cm^{-1} loses the stability in its spectral position upon variation in sulfite concentration with a spectral position shifting value of $\pm 12 \text{ cm}^{-1}$ at its maxima for reasons not identified. **Figure 1** shows the superimposed qualitative and quantitative IR absorption spectra at different levels of sulfite in the region of 1100–400 cm^{-1} . Although the IR peak observed at 495 cm^{-1} is relatively less strong at high sulfite concentration compared to the peaks at 973 and 633 cm^{-1} , due to its consistency in spectral position and quantitative behavior, this peak at 495 cm^{-1} for the S–O bending vibration (ν_4) was chosen for the quantitative determination of sulfite in the pure compound and in the real samples. The calibration curve method was used for the analysis. The calibration curve method uses the Lambert–Beer law and executes the quantification of an unknown sample by acquiring a regression equation, which represents the relationship between the peak intensity (peak height or absorbance) or peak area in absorbance mode of target ion and concentration from spectra of standard samples for which concentrations are already known. A two-point baseline correction for quantification of the sulfite is done in the spectral range of 520–470 cm^{-1} .

Structural Chemistry of Sulfite (SO_3^{2-}). Sulfite (SO_3^{2-}) has a pyramidal structure in its free form, and this ion may coordinate to a metal as a unidentate, bidentate, or bridging ligand. The following two structures are probable for unidentate coordination.



The C_{3v} symmetry of the free ion will be presented if coordination occurs through sulfur. If coordination occurs through oxygen, the symmetry may be lowered to C_s . In this case, the doubly degenerate vibrations of the free ion will split into two bands. It is reported that coordination through sulfur will shift the SO bands to higher frequencies, whereas coordination through oxygen will shift them to lower frequencies relative to those of the free ion. On the basis of these criteria, reports have been presented to show whether like metal groups will bind through the S-atom or O-atom of the sulfite (49). However, these results reported on lower and higher frequencies for S–O bonds based on S-atom or O-atom bonding of metals are studied

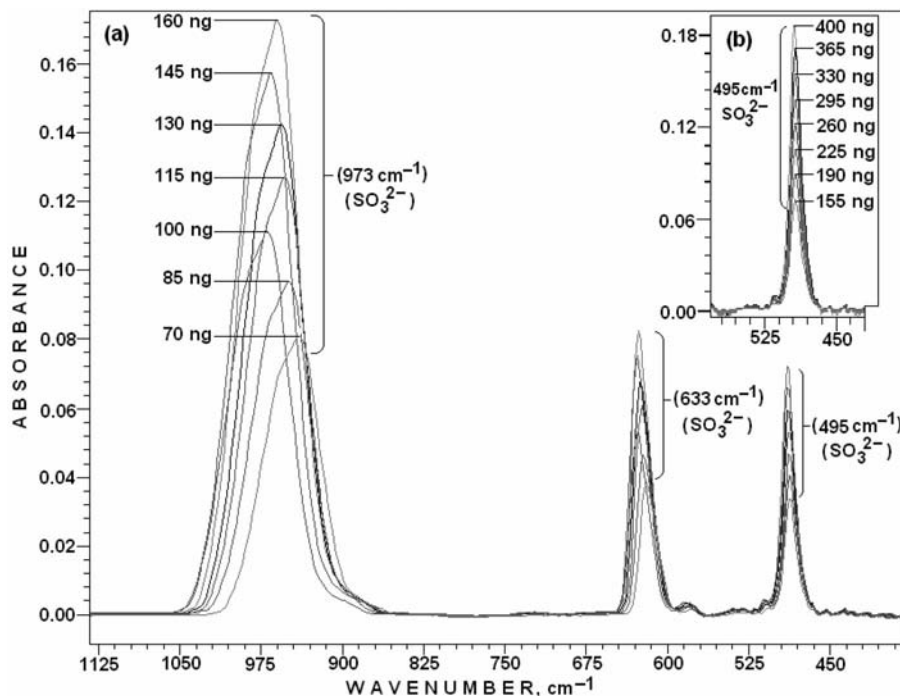


Figure 1. (a) Qualitative peak(s) at maxima 973, 633, and 495 cm^{-1} for sulfite obtained at different concentration levels of SO_3^{2-} spiked over 0.1 g of KBr: (1) 70 ng; (2) 85 ng; (3) 100 ng; (4) 115 ng; (5) 130 ng; (6) 145 ng; (7) 160 ng. (b) Quantitative IR reflectance spectra converted into Kubelka–Munk spectrum for smoothing of the baseline obtained at a broader concentration range of SO_3^{2-} at a different absorbance scale: (1) 155 ng; (2) 190 ng; (3) 225 ng; (4) 260 ng; (5) 295 ng; (6) 330 ng; (7) 365 ng; (8) 400 ng.

Table 2. Statistical Data for the Different Calibration Curves Prepared for the Wide Range of Sulfite Concentrations

calibration curve no.	concn range, ng SO_3^{2-} / 0.1 g of KBr	statistical data ^a for the x - y plot (concn vs absorbance and peak area) for the st line eq, $y = a + bx$								
		intercept (a)	slope (b)	st line eq ^b ($y = a + bx$)	correl coeff (r)	CD r^2	DF adj r^2	fit std err	F stat	RSD ($n = 8$) \pm %
1 ^c	50–5000	0.002	0.018	$C_{\text{SO}_3^{2-}} = 53.19\text{Abs} + 0.13$	0.999	0.999	0.996	0.001	10522.9	2.4
2 ^d	50–5000	0.010	0.244	$C_{\text{SO}_3^{2-}} = 4.09\text{Abs} + 0.04$	0.998	0.996	0.995	0.029	2959.5	2.2

^a Data processed by the software Table Curve 2D v 5.01.01. ^b $C_{\text{SO}_3^{2-}}$ = concentration of sulfite-ng/0.1 g of KBr; Abs = absorbance at quantitative peak; A_{peak} = area under the peak; CD = coefficient of determination (r -squared); DF adj r^2 = degree of freedom adjusted coefficient of determination; fit std err = fit standard error (root MSE); F stat = F statistic. ^c Data for full-range plot of sulfite concentration versus absorbance. ^d Data for full-range plot of sulfite concentration versus peak area.

for solid complexes where interatomic interactions are much more rigorous. In aqueous medium at very low sulfite concentration, however, this effect is possibly suppressed due to strong ionization of the dilute solution into free sulfite. In accordance with the above, in the present work, the spectral band position for S–O bending mode remained intact, and peaks observed at 633 and 495 cm^{-1} are akin to that reported earlier for the free sulfite ion. Hence, for real sample analysis absorption measurement was also carried out at 495 cm^{-1} . This constancy of the quantitative peak indicates the free S-atom of sulfite in the sample. Other peaks were not observable due to dilution factors in the real samples as discussed earlier.

Kubelka–Munk Spectrum and Calibration Curves. The equation shown below executes Kubelka–Munk conversion for a spectrum analyzed by the diffuse reflection method. This conversion is required to enable use of a reflectance spectrum measured by the diffuse reflection method for search of quantitative analysis.

$$f(R) = \frac{(1 - R)^2}{2R} = \frac{k}{s}$$

Here k = the molecular extinction coefficient, s = the scattering coefficient, and R = reflectance (power spectrum of sample/power spectrum of dilution material, KBr).

The Kubelka–Munk conversion uses the formula above to invert a reflectance spectrum measured by the diffuse reflection method into a quasi-quantitative spectrum that correlates with the concentration of the sample.

Dealing with a wide range of concentration is the magnificence of the FTIR technique. Therefore, the calibration curves for peak height and peak area were prepared by making use of the respective Kubelka–Munk spectrum obtained for the minimum and maximum sulfite concentration range, in the concentration ratio 1:100, of the equivalent amount of sulfite in the same ratio. The software IR Solution, housed with the basic equipment, converts automatically the reflectance spectrum into the Kubelka–Munk spectrum for smoothing of the baseline (Figure 1). The data on full range of the concentration were plotted against the respective absorbance values, calibration curve number (CC 1). The corresponding absorbance data were obtained at 495 cm^{-1} for a large number of standard series with as little as 50 ng of SO_3^{2-} /0.1 g of KBr and as high as 5000 ng of SO_3^{2-} /0.1 g of KBr. The absorbance data obtained for the Kubelka–Munk spectrum were processed by the software Table Curve 2D v 5.01.01, Systat Software Inc.). This absorbance versus concentration plot shows a straight line with an excellent correlation coefficient value of 0.999. The slope and the intercept for this straight line were 0.018 and 0.002, respectively.

Table 3. Determination of Sulfite Levels in Beverage Samples Analyzed by the Present DRS-FTIR Method and the Reported Ion Chromatographic Method

sample	amount of SO ₃ ²⁻ found			
	present method (DRS-FTIR) ^a		earlier reported method (IC) ^b	
	concn, $\mu\text{g}/\text{mL}$	rel std dev ($n = 6$), %	concn, $\mu\text{g}/\text{mL}$	rel std dev ($n = 3$), %
wine (white)				
1	112.9	5.0	115.1	5.4
2	123.1	5.1	125.6	5.1
wine (red)				
1	135.2	7.8	132.4	6.3
2	140.2	6.7	143.7	4.6
beer				
1	75.3	3.5	73.4	2.3
2	55.6	2.4	53.6	0.9
orange juice				
1	160.4	2.5	164.4	1.0
2	184.1	3.0	181.1	1.2
lemon juice				
1	119.2	2.7	116.2	2.6
2	114.3	3.4	112.3	3.4

^a Diffuse reflectance Fourier transform spectroscopic method. ^b Ion chromatographic method (51).

The peak area is also a significant parameter for the quantification of sulfite. In much the same way as discussed above, the full range of concentration (50–5000 ng of SO₃²⁻/0.1 g of KBr) was also plotted against the respective peak areas obtained for a series of full concentration range (CC 2). The peak area data obtained for the Kubelka–Munk spectrum showed excellent linearity for this curve also with correlation coefficient, slope, and intercept values for the straight line equation $y = mx + c$ as 0.998, 0.244, 0.010, respectively.

Table 2 shows some other significant statistical data for CC 1 and CC 2 along with the calibration curve equations. In addition to the correlation coefficient values as discussed above, four more statistical parameters such as coefficient of determination (r^2), degree of freedom adjusted coefficient of determination (DF adj r^2), fit standard error (fit std err), and F statistics (F stat) were also obtained for two sets of X – Y data. These

parameters are the measure of dependency between the two data sets for the regression lines. As a general understanding, as a straight line fit turns out to be more ideal, the r^2 and DF adj r^2 values approach 1.0 (0 represents a complete lack of fit), the fit std err decreases toward 0, and the F stat goes toward infinity. These parameters as obtained are 0.999, 0.996, 0.001, and 10522.9, respectively, for CC1 and 0.996, 0.995, 0.029, and 2959.5, respectively, for CC 2. Thus, the data shown in **Table 2** verify the ideal rank of the calibration curves, CC 1 and CC 2.

Analytical and Statistical Parameters. Instrumental analytical parameters, such as the detection limit and limit of quantification, and the statistical parameters for precision analysis, such as standard deviation and relative standard values, were also calculated. The limit of detection (LOD) and the limit of quantification (LOQ) (50), the standard deviation, and the relative standard deviation of the method were calculated for sulfite CC 2. The LOD of the method is calculated to be 8 ng of SO₃²⁻ 0.1 g⁻¹ of KBr substrate. The LOQ value is calculated to be 40 ng of SO₃²⁻ 0.1 g⁻¹ of KBr substrate. The linear range of the method (LR) and the LOD based on the concentration of sulfite in the solution are 5–500 and 0.8 $\mu\text{g}/\text{mL}$, respectively. The standard deviation value and the relative standard value at a level of 100 ng of SO₃²⁻/0.1 g of KBr for $n = 10$ are found to be 2 ng of SO₃²⁻ and 2.3%, respectively. The mean ($n = 10$) microdrop volume is 10.1 μL , calculated by mass difference method, indicating the uncertainty in drop volume in terms of standard deviation (sd) to be 10.1 ± 0.2 (mean \pm sd) μL . The test solution containing 100 ng/10 μL of SO₃²⁻ would then carry an uncertainty in concentration of 2 ng of SO₃²⁻. This will ultimately carry a small concentration uncertainty of 2% in the final result. This is also indicated by the comparable relative standard deviation value as calculated to be 2.3% for $n = 10$ as above.

Effect of Foreign Species. For study of the interionic effect on the change in the position of spectral band and intensity for standard sulfite a large number of inorganic and organic multiatomic anionic and cationic chemical species were tested. The interionic effect of foreign species was checked using the quantitative IR peak at 495 cm⁻¹ at a level of 100 ng of SO₃²⁻ contained in a single drop of test solution, which is equivalent to a volume of 10 μL , and sprayed over 0.1 g KBr matrix. In

Table 4. Comparison of Analytical Features of Different Techniques Used for Measurement of Sulfite

technique	linear range	detection limit	reagents used	ref
spectrofluorometry	5–800 ng/mL	1.4 ng/mL	polyoxyethylene sorbitan monooleate (Tween 80), citric acid–phosphate buffer, phosphate buffer, sulphite.	2
fluorometry	0.01–0.4 $\mu\text{g}/25$ mL 1.31–26.2 mg/L	0.01 $\mu\text{g}/25$ mL		12 13
spectrophotometry	0–6 $\mu\text{g}/7.5$ mL 0–26 mg/L	0.1 $\mu\text{g}/7.5$ mL 1.0 mg/L	bromine, methyl red	14 16
phosphorescence chromatography	10 $\mu\text{mol}/\text{L}$ –1 mmol/L 5 $\mu\text{mol}/\text{L}$ –1.0 mmol/L	10 $\mu\text{mol}/\text{L}$	mono bromobimane (3,7-dimethyl-4-bromomethyl-6-methyl-1,5-diazabicyclo[3.3.0]octa-3,6-diene-2,8-dione), acetonitrile, methanol, 4-(2-hydroxyethyl)-1-piperazineethane-sulfonic acid buffer	22 24
	0.02–400 $\mu\text{g}/\text{mL}$		sodium carbonate, sodium hydrogen-carbonate, 1,3,5-benzenetricarboxylic acid (BTA), cerium, sulphuric acid	27
electrochemistry	0.25–15 mg/L 01.015–25 mg/L	0.05 mg/L	phosphate buffer and phenyl arsineoxide (PAO)	28 29
enzymatic technique	0.002–0.3 mmol/L	0.001 mmol/L		31
chemiluminescence	0.05–10 mg/L 0–30 mg/L	0.03 mg/L 3 mg/L	Rhodamine 6G Tween 80	32 35
DRS-FTIR technique	50–5000 ng/10 μL or 5–500 $\mu\text{g}/\text{mL}$	8 ng/0.1 g of KBr matrix or 0.8 $\mu\text{g}/\text{mL}$	reagentless	present method

addition to the standard sulfite solution spiked over KBr matrix, varied known amounts of the foreign species were also introduced, and the matrix was then analyzed as in the procedure. The band position and spectral intensity of sulfite remained unchanged even in the presence of at least a 150-fold molar excess of the following tested multiatomic cationic and anionic species: NH_4^+ , CN^- , OH^- , SCN^- , NO_2^- , ClO_2^- , NO_3^- , ClO_3^- , ClO_4^- , BrO_3^- , IO_3^- , IO_4^- , HCO_3^- , MnO_4^- , CO_3^{2-} , SeO_3^{2-} , AsO_3^{2-} , MoO_4^{2-} , FeO_4^{2-} , CrO_4^{2-} , $\text{Cr}_2\text{O}_7^{2-}$, SiO_4^{2-} , BO_3^{3-} , PO_4^{3-} , AsO_4^{3-} , formate, acetate, oxalate, succinate, cinnamate, and citrate. Equal amounts of HSO_3^- and HSO_4^- interfere strongly, due to similarity in the structure. Interestingly, however, SO_4^{2-} interferes at all spectral positions as is observed for SO_3^{2-} , except at 495 cm^{-1} (46). Monoatomic cations and anions such as Na^+ , K^+ , Ca^{2+} , Mg^{2+} , Cl^- , Br^- , I^- , and F^- have absolutely no diverse effect in the quantitative determination of sulfite because they do not possess dipole change; however, their effects are seen only below 200 cm^{-1} .

Determination of Sulfite in Beverage Samples. Sulfite determination was done in three alcoholic and two nonalcoholic beverage samples. Red and white wines, beer, and orange and lemon juice samples available in the local market were tested for the quantitative determination of sulfite. In beverage samples such as the fruit juices, in addition to sulfites, mixtures of ascorbic, malic, citric, etc., acids are also added as preservatives. Thus, to prevent loss of the analyte by volatilization as SO_2 on acidification of sulfite and to determine total sulfite, alkaline hydrolysis was done by the addition of an excess amount of NaOH (0.05 mL, 0.1 M)– H_3BO_3 (0.2 mL, 0.1 M) buffer to the 1 mL volume of sample so that the final pH of the sample remained above 8.5. The NaOH – H_3BO_3 buffer was added to the sample immediately after the sample can was opened. A single drop (10 μL) of this prepared beverage was then poured onto preweighed 0.1 g of KBr substrate. Then the KBr matrix, containing the sample, was dried in a water bath at a temperature of around $40\text{ }^\circ\text{C}$ for 3 min. After drying, KBr matrix was ground to fine particles with the use of an agate mortar for 1–2 min and thoroughly mixed. This sample was put in the sample holder of the DRS attachment and analyzed by the FTIR, and absorption measurement was done at 495 cm^{-1} as in the procedure described earlier.

In all of the tested real samples there was no need of any dilution or preconcentration steps, because the actual contents found were well within the analysis range of sulfite as done in the preparation of standard calibration curves for sulfite determination.

The relative standard deviation, for a set of six determinations in each case, was found to be in the range of 2.4–7.8% (Table 3). The results of the present method were also compared to those of the ion chromatographic method (51), and the data are in close agreement (Table 3).

The applicability of the DRS-FTIR technique has been demonstrated for the quantitative determination of the sulfite in both alcoholic and nonalcoholic beverages. Highly satisfactory results were obtained. The proposed method is extremely rapid because once the substrate sample is prepared, spectral information regarding absorbance and peak area values may be obtained within 10 s. Thus, the method has a high sample throughput value. Use of tremendously reduced sample size is the magnificence of this method. Thus, although the LR and LOD of the method are comparable to those of the earlier reported methods (Table 4), the present method is of particular importance when the sample available for analysis is at microliter size. Reagentless analysis and low detection limit value also

add to the beauty of this method, which also supports the need of green chemistry research. Comparison of characteristic features of some of the earlier reported methods and the present method is shown in Table 4, which shows the suitability of the present method.

ABBREVIATIONS USED

DRS-FTIR, diffuse reflectance Fourier transform infrared spectroscopy; LOD, limit of detection; LOQ, limit of quantification; LR, linear range; DTGS, deuterated triglycine sulfate.

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