

Gas-phase Molecular Absorption Spectrometry: Determination of Sulphite with Diode-array Detection

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Abstract. A method is described for determining sulphite by SO₂ generation and UV-visible molecular absorption spectrometry with diode-array detection. The molecular absorption maximum of SO₂ appears at 198 nm. The parameters affecting generation (particularly those relating to the kinetics of the process) and determination are optimized; under the optimum conditions found, only a 30 s preconcentration time is necessary. The linear response range is between 10 and 1000 µg ml⁻¹ of SO₃²⁻, the RSD is 3.5% and the detection limit is 3.2 µg ml⁻¹. The effect of different species on the SO₂ signal is also studied. The method is applied to the determination of SO₂ in air samples.

Key words: sulphite, UV-gas phase, molecular absorption spectrometry, air samples.

Sulphite appears in many kinds of sample at levels lower than can be determined using classical procedures [1]. However, there are now many instrumental methods for sulphite determination, such as electro-analytical methods (potentiometric [2, 3] or amperometric [4, 5]) and optical methods (molecular emission cavity analysis [6], molecular fluorescence [7], emission by inductively coupled plasma [8] or chemiluminescence), but the most widely employed is UV-Vis molecular absorption spectrometry (MAS) based on indirect procedures.

When sulphite is determined directly by MAS, a prior separation step is commonly required (using liquid chromatography or capillary electrophoresis

[9]), because there are several chemical species that absorb in the same region of the UV spectrum as sulphite. It is possible to make use of indirect procedures based on complex formation, which can be measured spectrophotometrically; some reagents employed are nitroprussate, tetrachloromercurate or pararosaniline [10]. However, the most frequently used methods are based on a prior redox process, mainly using two alternatives: (1) transformation of sulphite to sulphide using a reducing agent, sodium tetrahydroborate [11] for example, and subsequent determination of sulphide; (2) oxidation of sulphite and determination of the reaction product (sulphate) or the excess oxidant agent employed [12].

A very interesting alternative is the use of methods based on SO₂ generation and measurement of the volatile, although the instrumentation and methodology employed to date have suffered from complexity [13]. A technique based on volatile generation is gas phase molecular absorption spectrometry. The first papers on this technique were published by Cresser and Syty, independently. Sulphur species were determined by H₂S or SO₂ generation [14–18].

In this paper, sulphite determination by SO₂ generation and subsequent measurement of the molecular absorption of the volatile compound with a diode-array spectrophotometer is proposed; the method is faster, simpler and more sensitive than others based on SO₂ generation. This technique has already been employed by us for other sulphur species, ammonium and hydride-forming elements determination; all these procedures have been recently reviewed [19]. The technique is also employed as a detector for gas chromatography [20].

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Experimental

Apparatus

All measurements were performed with a Hewlett-Packard Model HP8451A diode-array spectrophotometer, equipped with a HP98155A keyboard (Hewlett-Packard), a floppy disk drive for bulk data storage (Hewlett-Packard HP9121), and a graphics plotter (HP7475A). A Hellma 174QS flow cell (path length 1 cm) was used.

A MacLeod air sampler, equipped with a flow-meter, a 0.45- μm pore Teflon filter and 50 ml of 0.1 M NaOH solution was used to sample the gaseous emissions.

Reagents

All reagents used were of analytical grade quality.

Standard sulphite solution was prepared by dissolving $\text{Na}_2\text{SO}_3 \cdot 7\text{H}_2\text{O}$ in a 5% glycerine – water solution as stabilizer. Working standards were prepared by serial dilution of the stock solution with twice-distilled water, immediately before use.

Concentrated sulphuric acid (1.84 g ml^{-1}); working standards were prepared by diluting the concentrated solution with water.

Volatile Generation

Sulphur dioxide was generated using a simple generation system, as previously described [21] for sulphide determination; in this study a 25-ml Erlenmeyer flask was employed as the generation vessel.

To generate SO_2 , 0.5 ml of concentrated sulphuric acid are added to the generation vessel, which is then sealed and connected to the nitrogen flow (700 ml min^{-1}); in such conditions, a reference measurement is performed. Then the nitrogen flow is stopped and the exit of the volatile is closed; 1 ml of sulphite solution is injected and 30 s later the nitrogen flow is opened again and the generated volatile is transported to the flow cell. This gives better results than generation procedures based on the injection of acid into a sulphite solution.

Measuring Peak Height

The passage through the spectrophotometer of the compound generated can be followed by programming the instrument with a Basic program [22], which records a molecular absorption spectrum from 190 to 240 nm every 0.2 s during a total time of 8 s (Fig. 1).

In order to quantify the amount of sulphide dioxide generated, another Basic program was used which permits measurement of the absorbance at a fixed wavelength every 0.1 s (in this case 198 nm, the maximum of the molecular absorption spectra) and which represents absorbance versus time. Peak height and peak area values of the transient signal were obtained, but better reproducibility was obtained when peak height was used as the quantification parameter.

Results and Discussion

The optimum values of the different parameters affecting the generation and determination of sulphur dioxide were studied and optimized: carrier gas flow,

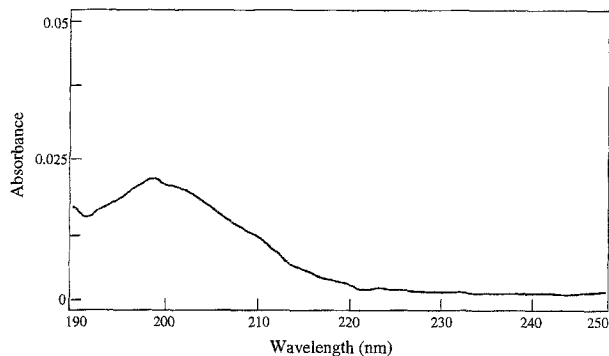


Fig. 1. SO_2 molecular absorption spectrum

preconcentration time, acidity of the medium and total volume of the sample. The peak height of the transient signal was used throughout.

Perhaps the most significant inconvenience in this determination is the low SO_2 generation speed. In order to improve the signal and the yield of the process, different alternatives were tested: (a) generation at temperature above ambient, (b) use of a stirrer, (c) preconcentration of the volatile during the generation process and (d) addition of a substance capable, in an acidic environment, of forming a gas which acts as internal carrier. We have used alternative (d) previously for hydrogen sulphide generation [21] with NaBH_4 (which decompose in acid medium to liberate hydrogen gas). In this case it is not possible to use NaBH_4 because this compound reduces sulphite to sulphide; another alternative compound tested was sodium carbonate, but interference problems were observed. In this work, the best results were obtained by using alternative (c). In this case, sulphite and acid solutions were mixed into the generation vessel and the flow of carrier gas closed off. Then the generation vessel was hermetically closed as SO_2 was forming. After a preconcentration time, the volatile was transported to the flow cell.

Preconcentration time is defined as the time from when sulphite solution is injected into the generation flask to the moment when the SO_2 generated is transported to the spectrophotometer flow-cell; the effect of this parameter on the analytical signal can be observed in Fig. 2. The optimum value was 30 s; a shorter time did not allow for complete generation, while a longer time could mean signal loss due to dispersion by diffusion.

Hydrochloric, perchloric and sulphuric acids were tested in order to obtain optimum acidity of the medium. The best signal/noise ratio was obtained by

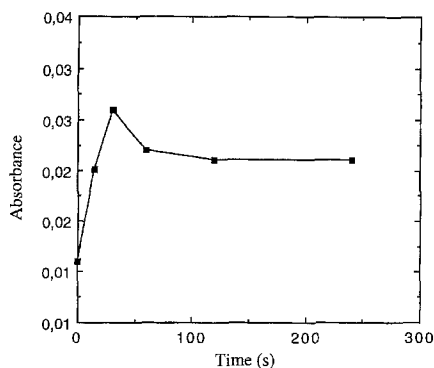


Fig. 2. Variation of SO₂ absorbance (peak height) at 198 nm vs. pre-concentration time

using sulphuric acid. In order to obtain the best concentration and volume of sulphuric acid, three types of studies were performed, using the same sample volume in all cases:

(1) Sequential study of the concentration (from concentrated to 6 M); concentrated acid gave the best results; with a sharp decrease in the signal as the concentration was decreased.

(2) Sequential study of the volume (ranging between 0.25 and 5 ml). Using volume ≥ 2 ml of concentrated acid, a considerable blank signal was produced, whereas volumes of less than 0.5 ml were insufficient to generate SO₂ completely. Blank signals were caused by water carry-over into the flow cell.

(3) As the efficiency of SO₂ generation depends simultaneously on the concentration and the volume of the acid, a combined study of these two variables was performed (maintaining a constant quantity of acid in the generation flask). Optimum values were obtained by working with small volumes and high concentrations. This is logical, because decreasing the acid concentration slows the reaction and a longer time is therefore required to produce the gas separation from the liquid phase.

In conclusion, the optimum volume and concentration were 0.5 ml of concentrated sulphuric acid.

The effect of the volume of sample solution in the generation flask was also studied, keeping the total amount of sulphite constant; optimum values were obtained using 1 ml. Volumes bigger than 1 ml did not produce greater peak heights and volume smaller than 1 ml cannot be recommended, because although the absorbance value was high, the sensitivity (expressed as peak height/concentration) was poor.

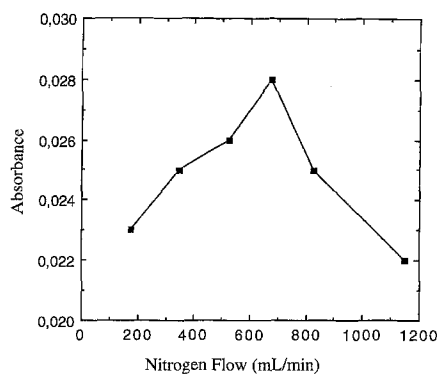


Fig. 3. Variation of SO₂ absorbance (peak height) at 198 nm vs. nitrogen flow

The influence of carrier gas flow-rate is shown in Fig. 3. When the flow-rate is low, the gas reaches the cell slowly and the peak area increases. On the other hand, high flow-rates greatly dilute the volatile, so that the peak height and area are reduced. When a nitrogen flow-rate of 700 ml min⁻¹ was used, the best signal resolution and a satisfactory value of the maximum absorbance were obtained.

Table 1 summarizes the best conditions for SO₂, both for its generation and its determination by gas-phase molecular absorption spectrophotometry.

Linear Range, Reproducibility and Detection Limit

Under the optimum conditions for sulphur dioxide generation, the relative standard deviation (RSD) of 10 replicate determinations of 50 $\mu\text{g ml}^{-1}$ sulphite was 3.5% for peak height. The method gives a linear response from 10 to 1000 $\mu\text{g ml}^{-1}$ sulphite and the detection limit is 3.2 $\mu\text{g ml}^{-1}$, calculated from the sensitivity and standard deviation of the blank measurement ($k=3$).

Interference Study

The effect of different species of sulphur on the SO₂ signal was studied. Sulphide shows a large positive

Table 1. Optimum conditions for SO₂ determination by GPMAS

Wavelength	198 nm
Preconcentration time	30 s
Sample volume	1 ml
Acidity	0.5 ml, conc. H ₂ SO ₄
Nitrogen flow	700 ml min ⁻¹
Generator	25 ml Erlenmeyer

Table 2. Results obtained on air samples

Day	Thorin ($\mu\text{g m}^{-3}$)	GPMAS ($\mu\text{g m}^{-3}$)
1	250	230
2	220	210
3	300	280
4	280	290
5	260	260

interference in 1:1 (*m/m*) (interference/sulphite) ratio, because of H_2S generation. Thiocyanate (10:1) increases the signal by 15%, possibly due to SCO generation. Thiosulphate (1:1) interferes by 47% and persulphate (1:1) decreases the SO_2 signal by 50%, because it oxidizes sulphite to sulphate. At least 2000:1 sulphate, nitrate, chloride or perchlorate do not disturb the analytical signal for sulphite. Except for sulphate, it is very difficult to find real samples with a high content of sulphur anions with respect to sulphite, so these interferences will not appear in the most determinations; in addition, the presence of these interferences (except persulphate) could be detected if the molecular absorption spectra of the sample is obtained.

Application

In order to check the method, sulphite (as sulphur dioxide) was determined in air samples by using a MacLeod sampler in the city of Zaragoza. About 3.0 m^3 of air was bubbled into 50 ml of NaOH solution (over approximately 24 h). This solution was then made up to 50 ml again and analysed following our procedure. A second MacLeod sampler (with 50 ml of H_2O_2 solution) was installed in order to analyse the

samples by a reference method (precipitation volumetric with Ba(II) and thorin as indicator). The results obtained (Table 2) by the proposed method on five days agreed with those of the reference method.

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