Spectrophotometric flow-through sensor for the determination of sulphur dioxide

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Abstract

A continuous-flow sensor based on integrated separation and spectrophotometric detection was developed for the determination of sulphur dioxide at the ng ml^{-1} level by transient immobilization of the reaction product formed between *p*-rosaniline, formaldehyde and sulphur dioxide on an ion exchange support packed in a flow cell. Sulphur dioxide was thus determined in the range 0.16–6.0 $\mu g\ ml^{-1}$ with a relative standard deviation of 2–3% ($n = 11$). The detection limit (3σ) achieved was 49 ng ml^{-1}. The proposed sensor was applied to the determination of free sulphur dioxide in white and rosé wines and the results obtained were consistent with those provided by the EEC recommended method.

Keywords: Flow injection; Sensors; UV–Visible; Sulphur dioxide; Wines

The use of sensors in continuous-flow systems reportedly enhances valuable analytical features of both manual and flow methods using the same analytical reaction [1–3]. The sensitivity and selectivity can be dramatically improved through the in situ concentration and separation processes taking place simultaneously on a support packed in the flow cell of a flow-through (bio)chemical sensor. These sensors are based on immobilization of one of the components of a (bio)chemical reaction in a flow cell packed with a suitable support that is placed in the light path of a molecular spectroscopic detector. The different systems developed so far in this context can be classified according to where the analytical reaction takes place along the manifold (the reaction can be homogeneous or heterogeneous depending on whether it is carried out previously or in the flow cell, respectively). The analytical reaction can take place at: the support–solution interface [4–6] when the analyte or the reagent is the species to be immobilized in the flow cell, the catalyst–solution interface [7,8] when the catalyst, usually an enzyme, is to be immobilized or in the reactor, between the injection and detection units, when the support is to retain the reaction product [9–12]. The last approach was used in this work for the determination of sulphur dioxide by measuring the absorbance increase resulting from retention of the reaction product yielded by *p*-rosaniline–formaldehyde and sulphur dioxide in a flow cell packed with an ion-exchange resin.

Various conventional methods have been used to determine SO_2 in different types of samples [13–17], most of which have some pitfalls as regards sensitivity, selectivity or simplicity. Flow-injection (FI) methods were recently applied to the determination of sulphur dioxide by using different manifolds and detection systems [18–23], all of which showed the high potential of FI for the

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determination of this analyte. However, no integrated retention–detection sensor for the determination of SO_2 has so far been reported. This paper reports on the analytical advantages and the features of this approach for the determination of this analyte and on its application to wine analyses.

EXPERIMENTAL

Reagents

An amount of ca. 0.100 g of anhydrous sodium sulphite was dissolved in 100 ml of doubly distilled water. This solution was standardized iodimetrically and more dilute solutions were prepared from it as required. Fresh solutions were prepared daily and stabilized with morpholine (0.01%) [16,17]. A 0.2% *p*-rosaniline (PRA) aqueous solution in 1 M HCl was prepared and purified according to Scaringelli et al. [13]. A 0.4% formaldehyde solution was prepared daily.

The eluent was 2 M HCl saturated with butan-1-ol. The anion-exchange material was rinsed with doubly distilled water and conditioned by triplicate treatment with 4 M HCl, 2 M sodium hydroxide and doubly distilled water, which converted the resin into its chloride form [24].

A Hellma 138-OS flow cell (inner volume 40 μl) was packed with resin up to 5–8 mm from the bottom. For proper packing of the resin the carrier solution was passed through the cell for 5–10 min.

Apparatus and instruments

A Unicam Model 8625 UV–visible spectrophotometer equipped with the above-described flow cell and connected to a Knauer *x-t* recorder was used. A laboratory-made assembly including a planar BK7 PCX quartz lens driven by two micrometric screws was placed in the cell compartment in order to focus the light beam precisely at the exact position on the resin. The manifold used consisted of a Gilson Minipuls-2 four-channel peristaltic pump furnished with a rate selector, a Rheodyne Model 5041 injection valve, a Rheodyne Model 5060 rotary switching valve and a Tecator TM III chemifold.

RESULTS AND DISCUSSION

The manifold used is depicted in Fig. 1. A 2-ml sample volume was inserted into a doubly distilled water or buffered stream at a flow-rate of 1 ml min^{-1}. The stream was merged at point M with the reagent solution (0.08% PRA + 0.2% HCHO, pH 0.4) at a flow-rate of 1 ml min^{-1}. The reaction product formed (*p*-rosanilinemethylsulphonic acid) in mixing coil r (300 cm × 0.5 mm i.d.) was retained by the flow cell, packed with Dowex 1-X8 of 200 mesh anion exchanger, when the switching valve (SV) was in position 1. As the plug tail reached the detector (55 s after injection), the concentrated retained reaction product was readily eluted with 2 M HCl saturated with butan-1-ol, which was inserted via SV (position 2), thereby restoring the baseline.

Injection of samples directly into the eluting carrier (2 M HCl) streams resulted in irreproducible signals because the pH difference between sample and carrier could not be offset by merging with the reagent stream.

Types of signal

Two different types of signal were obtained depending on the order in which valves IV and SV (Fig. 2) were switched. The baseline was established while the eluting agent was circulated through the cell. When SV was switched to position 2, the absorbance signal increased to a con-

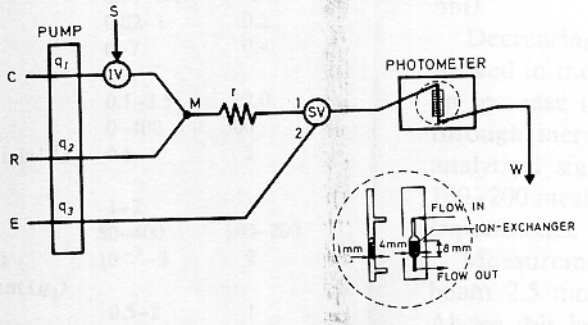

Fig. 1. Manifold used. S = sample; C = carrier; R = reagent (0.08% PRA + 0.2% formaldehyde, pH 0.4); E = eluent (2 M HCl saturated with butan-1-ol); q = flow-rate; IV = injection valve; M = mixing point; r = reaction coil; SV = switching valve; W = waste.

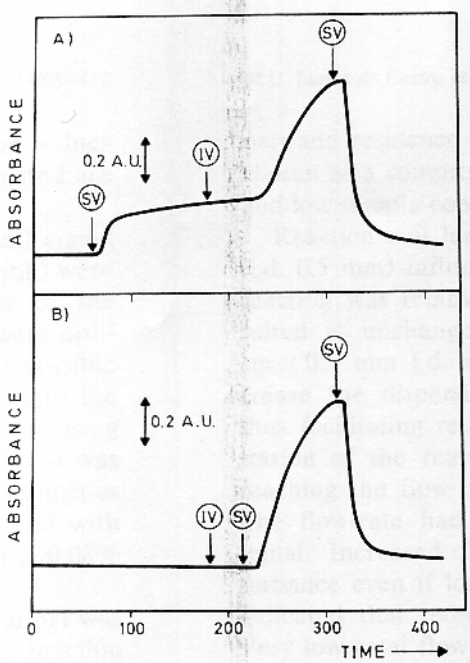

Fig. 2. Types of signal obtained according to the order in which SV and IV (switching and injection valve, respectively) were switched. For details, see text.

stant value of 0.18 on passage of the reagent through the cell (Fig. 2A). Then the sample was inserted via IV and a signal proportional to the concentration of SO_2 in the sample was obtained 60 s after injection. The other possibility (Fig. 2B), which was ultimately chosen, was to inject the sample by first switching IV and, after 55 s, also switching SV when the retention product arrived at it, thus allowing simultaneous recording of the signals corresponding to the reagent and retained reaction product. Therefore, the reagent contribution to the overall signal corresponded to the blank. In both instances, the eluent was inserted via SV after the tail portion of the plug had reached the flow cell, so the signal was rapidly returned to its baseline.

Optimization of the proposed method

The variables affecting the performance of the proposed method were divided into three groups: chemical, FIA and those typical of the retention–elution/detection unit (i.e., characteristic of the sensor). All variables were optimized by the univariate method; the optimum values and ranges over which they were investigated are given in Table 1.

Chemical variables. Both the analytical signal and the absorbance yielded by PRA (blank) were affected by the chemical composition of the reagent stream. Hence these variables were optimized in order to obtain the maximum possible analyte-to-blank ratio. Both contributions to the total peak were found to increase with increasing PRA concentration. Prior to optimization, it was essential to purify PRA [13] because impurities significantly increased the blank compared with the analyte signal. A PRA concentration of 0.08% was selected as optimum.

A similar effect of the reagent stream pH was observed. The colour intensity of the reaction product was enhanced by an increase in pH (that of the reagent stream was also pH dependent). The optimum pH was 0.4. On the other hand, no significant absorbance was obtained at low formaldehyde concentrations. The absorbance increased with increasing concentration of formaldehyde up to a maximum value of 0.14%, above which no effect on the blank signal was observed. A concentration of 0.2% of formaldehyde was selected as optimum.

FIA variables. Increased sample volumes resulted in proportionately increased analytical sig-

TABLE 1

Study of variables

Variable	Range studied	Optimum value
Chemical		
PRA (%)	0.01–0.16	0.08
Formaldehyde (%)	0.02–1	0.2
pH	0–7	0.4
FIA		
Injected volume (ml)	0.1–3.5	2.0
Reactor length (cm)	0–400	300
Flow-rate ($q_1 + q_2$) (ml min^{-1})	0.5–4	2
Retention–detection unit		
Path length (mm)	1–2	1
Particle size (mesh)	50–400	100–200
Eluting agent (HCl) (M)	10^{-3}–3	2
Flow-rate of eluting agent (q_3) (ml min^{-1})	0.5–2	1

nals and residence times. A volume of 2 ml was chosen as a compromise between high sensitivity and low sample consumption.

Reaction coil lengths between 0 and 190 cm (i.d. 0.5 mm) influenced the peak height as the reaction was relatively slow. Longer lengths resulted in unchanged signals. A reactor of 300 cm × 0.5 mm i.d. was adopted in order to increase the dispersion of the reaction product, thus facilitating retention by fitting the concentration of the reaction product in the solution reaching the flow cell to the retention kinetics. The flow-rate had a marked influence on the signal. Increased flow-rates decreased the absorbance even if long reactors were used, which indicated that retention was not instantaneous. Very low total flow rates (0.5 ml min^{-1}) yielded very high yet irreproducible signals; hence an optimum value of 2.0 ml min^{-1} was chosen as a compromise between high sensitivity, reproducibility and sample throughput.

Variables of the retention–elution / detection unit. The influence of the cell path length was studied with cells of 1.0, 1.5 and 2.0 mm path length. The absorbance increased in proportion to the path length, but the resin itself saturated the detector capacity when cells of 2.0 mm were used. A cell of 1.0 mm path length yielding a baseline absorbance of 1.300 was chosen for all subsequent experiments.

The reaction product (*p*-rosanilinemethylsulphonic acid) yielded an absorption spectrum with maximum absorbance at 558 nm in solution, and was readily immobilized on anionic Dowex 1-X8 resin under the above-described working conditions (see Experimental), its maximum absorption wavelength being slightly shifted to 560 nm).

Decreasing the particle size of the support packed in the flow cell (50–400 mesh) resulted in an increase in the absorbance of the resin itself through increased compaction of the solid (the analytical signal remained constant). A resin of 100–200 mesh was chosen as optimum for further experiments.

Measurements were made by focusing the light beam 2.5 mm below the top of the resin level. Above this height, the signal decreased dramatically because the light beam passed through the solution above the resin. Heights lower than 2.5 mm decreased the absorbance at a rate of 0.05 mm^{-1} because the reaction product was largely retained on the resin zone where the flow impinged.

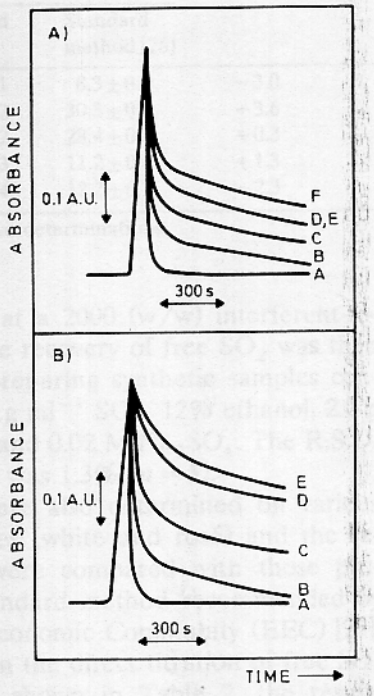

Fig. 3. Effect of various species used as eluting agents. (A) A, 2 M HCl; B, 30% ethanol; C, 30% dimethylformamide; D, E, 10% dimethylformamide and 20% ethanol; F, 10% ethanol. (B) Different concentrations of HCl: A, > 2 M; B, 1 M; C, 0.5 M; D, 0.01 M; E, 0.001 M.

The potential of different species as eluting agents for the reaction product retained on the resin was investigated in order to make the sensor regenerable. As can be seen in Fig. 3A, organic solvents were not efficient for rapid elution. However, increasing HCl concentrations improved the efficiency of the regeneration process and resulted in faster restoration of the baseline at concentrations above 2 M (Fig. 3B). The concentration finally chosen was 2 M. After long working periods, the time required for regeneration increased owing to the sorption of traces of impurities present in PRA after purification. This required using 2 M HCl saturated with butan-1-ol

as the eluent. In this medium, dye impurity traces were eluted in each regeneration step, thus making the system fully re-usable.

Features of the proposed method

A series of standards of concentration between 0.10 and 10.0 μg ml^{-1} were injected into the manifold under the optimum working conditions. The calibration graph obtained by plotting peak height against SO_2 concentration (Fig. 2B) was linear over the range 0.16–6.0 μg ml^{-1}. The corresponding equation obtained by the least-squares method was:

$$\text{absorbance} = 0.18 + 0.25[SO_2\ (\mu g\ ml^{-1})]$$

$$(r = 0.9998,\ \text{R.S.D.} = 2.4\%,\ n = 11)$$

The standard deviation of the blank absorbance and the limit of detection (3σ) were 0.004 and 49 ng ml^{-1}, respectively. Figure 4 shows the recordings obtained. At least 400 sequential determinations can be carried out with the same sensor.

Applications

Sulphur dioxide is added to wine in order to avoid undesirable oxidation reactions and also as an antiseptic agent. Its concentration in the wine must therefore be measured. The proposed method was applied to the determination of free sulphur dioxide in wine samples.

Common constituents of wine such as ethanol, tartaric acid and sodium sulphate were tested as potential interferents. Sodium sulphate was found not to interfere at a 2000 (w/w) interferent-to-analyte ratio. The recovery of free SO_2 was then determined by preparing synthetic samples containing 0.5–3.0 μg ml^{-1} SO_2, 12% ethanol, 2.0 g l^{-1} tartaric acid and 0.02 M Na_2SO_4. The R.S.D. of the recoveries was 1.3% ($n = 5$).

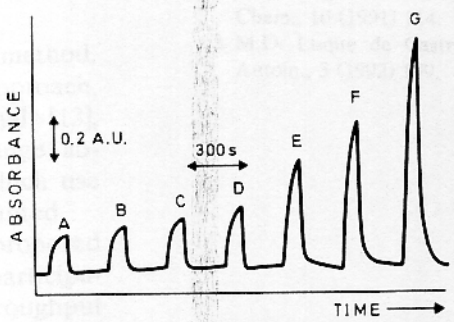

Fig. 4. Response signals from blank and increasing concentrations of SO_2. A, Blank signal; B, detection limit; C, determination limit; D, 0.43 μg ml^{-1}; E, 1.30 μg ml^{-1}; F, 2.15 μg ml^{-1}; G, 3.50 μg ml^{-1}.

TABLE 2

Determination of free sulphur dioxide in wines

Sample No.	Found [a]		Error (%)
	Proposed method	Standard method [26]	
1	8.0 ± 0.1	8.3 ± 0.9	−3.0
2	31.4 ± 0.2	30.3 ± 0.4	+3.6
3	28.5 ± 0.2	28.4 ± 0.5	+0.3
4	11.4 ± 0.3	11.2 ± 0.4	+1.3
5	12.0 ± 0.4	12.2 ± 0.3	−2.3

[a] Average ± s.d. of five determinations.

Recoveries were also determined on various real wine samples (white and rosé) and the results obtained were compared with those provided by the standard method recommended by the European Economic Community (EEC) [25], which is based on the direct titration of free SO_2 with iodine. As shown in Table 2, the results obtained by the two methods were consistent. The sensor cannot be applied to red wines because tannins are strongly retained by the support, giving spurious peaks.

Conclusions

A critical comparison of the proposed method, which is based on a sensor-integrated approach, with corresponding manual conventional [13], flow-injection [22] and batch ion-exchange absorptiometric counterparts [17], all of which use the same derivatization reaction, is warranted.

The most salient advantages of the proposed method are as follows: reduced human participation (automation capability); higher throughput than the batch alternatives (whether or not ion-exchange resins are used); high selectivity resulting from the in situ concentration kinetics; reusability of the resin, i.e., the sensor can be regenerated by elution of the retained reaction product (in the batch method, the resin is disposable); and simplicity, as reflected in the fact that

all the steps involved are performed in the flow system (the batch method requires manual mixing of the reactants, addition of the resin to the medium, washing, filtration and collection of the resin with the retained product in a conventional cell, followed by measurement).

On the other hand, the most serious disadvantage of the proposed sensor is its detection limit (49 nm ml^{-1}), which is higher than that of the batch ion-exchange method (5 ng ml^{-1}). This arises from absorption of the reactants prior to arrival of the product at the detector, i.e., from a high blank signal (see Fig. 4). Nevertheless, the proposed method is fifteen times faster than its batch counterpart, and is also simpler and involves much less human participation.

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