

Determination of SO₂ in Wines Using a Flow Injection Analysis System with Potentiometric Detection

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This paper describes the development and application of a flow injection analysis system manifold comprising a gas diffusion unit and a potentiometric detector to the determination of free and total SO₂ in white and red wines. A homogeneous crystalline iodide double-membrane tubular electrode was used as detector. SO₂ determination based on the Ripper method was carried out by dosing the iodide formed in the oxidation of SO₂ with iodine, followed by the separation of the formed compound through a diffusion Teflon membrane. The results obtained from the analyses of free and total SO₂ in 30 wine samples showed good agreement between the proposed method and the rapid assay method recommended by the UE and OIV. The relative error deviations of the results obtained by both methods were <6%. This procedure is suitable for samples with ~3.2–180 mg L⁻¹ SO₂, performing determinations of 75–100 samples h⁻¹.

Keywords: SO₂; flow injection analysis; wines; tubular electrode; increased sensitivity

INTRODUCTION

Sulfur dioxide is widely used as a wine preservative due to its antiseptic power and antioxidation effect (Ribereau-Gayon et al., 1976).

Before the wine is commercialized, this chemical parameter should be controlled both for its toxicity and for the changes of the organoleptic and chemical characteristics caused in the product before its consumption. Moreover, international regulation established a limit of total SO₂ present in wines, which compels its control. For the determination of SO₂ in wines, the EC has adopted a reference method based on dragging the sample with nitrogen or air, followed by fixation and oxidation of SO₂ in H₂O₂ solution, and titration of the sulfuric acid formed with standard NaOH solution (*Off. J. Eur. Communities*, 1990). Dragging and distillation procedures are widely recognized (Sullivan et al., 1990a) but are time-consuming and lack selectivity, sensitivity, and precision. For rapid control, the EC and Portugal suggested the iodometric procedure (*Off. J. Eur. Communities*, 1990), although this method has been strongly criticized (Vahl and Converse, 1980) because of its deficient selectivity in addition to its being rather slow. Moreover, as visual detection was used for the evaluation of the titration end point, it leads to low-precision results due to the wine color.

Several automated methods based on flow injection analysis (FIA) have been used for the determination of sulfite in wine. Spectrophotometry (Zhi et al., 1995; Richter et al., 1993; Linares et al., 1989; Lazaro et al., 1987; Falcone and Maxwell, 1992; Bartroli et al., 1991; Sullivan et al., 1990a,b; Maquiera et al., 1993), coulometry (Chen, 1995), amperometry/voltammetry (Rezende and Motolla, 1994; Thanh et al., 1994; Cardwell et al., 1991, 1993; Granados et al., 1986; Etherington, 1990; Krausova and Jedlickova, 1990), chemiluminescence

(Burguera and Burguera, 1988; Huang et al., 1992), and potentiometry (Marshall and Midgley, 1983; Badr et al., 1995) have been used as detection methods. The latter, according to the authors (Marshall and Midgley, 1983; Badr et al., 1995), is an advantageous alternative to the others because of its easy handling, selectivity, and precise measurements. However, there are some difficulties in implementing the aforementioned method in routine analyses, as the referred manifolds (Marshall and Midgley, 1983; Badr et al., 1995) used PVC membrane conventional electrodes with an inner reference solution (Badr et al., 1995) or air gap electrodes in a typical cascade system (Marshall and Midgley, 1983), resulting in mechanically unstable manifolds. Furthermore, the sample throughput was low as no more than 20 samples h⁻¹ were determined.

The development of iodide-sensitive electrodes (Couto et al., 1997), of simple construction and increased sensitivity, combines their capacity of being steadily adapted to flow systems with their improved response characteristics, namely signal stability, reproducibility, response rate, and easy handling.

An automatic system based on the FIA technique with potentiometric detection was developed for the determination of SO₂ in wines. An iodide-sensitive tubular electrode of simple construction and increased sensitivity, since it comprised two crystalline membranes, was used as detection system. The summing of the potentials of each membrane was performed by a summing device. Selectivity of determinations was increased by inserting a gas diffusion unit into the developed manifold. Therefore, a simple robust and economic manifold was attempted so that it could be used by any wine-making industry.

MATERIALS AND METHODS

Reagents and Solutions. All solutions were prepared with bidionized water (specific conductivity <0.1 μS cm⁻¹) and

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with reagents of analytical reagent grade without further purification.

The stock solution of 0.1 M Na₂SO₃ was obtained by carefully weighing the solid and was standardized daily by iodometric titration according to the method given in the *Off. J. Eur. Communities* (1990) and kept in the refrigerator before and after use. The SO₂ standard solutions were prepared daily from the previous solution by careful dilution before use and stabilized with glycerin (0.05% v/v).

The iodine solution used as titrant was prepared daily according to the method of Vogel (1988) by dissolving 12.5 g of potassium iodide in a minimum water volume and adding 6.35 g of iodine, standardized against a standard sodium thiosulfate solution, and kept in amber glass-stoppered bottles. The solution was afterward slowly diluted during the stirring procedure in an acetic acid/sodium acetate buffer solution (pH 4.3) to a 500 mL volume.

Apparatus. The potential was measured with a 2002 Crison potentiometer (sensitivity of ±0.1 mV) (Alella, Spain) connected to a BD 111 Kipp & Zonen recorder (Delft, The Netherlands).

The solutions were pumped by a Gilson Minipuls 2 peristaltic pump (Villier-le-Bel, France), and samples were inserted through a Rheodyne 5020 injection valve (Cotati, CA). The connection of all components of the FIA system was done with PTFE tubes (0.8 mm i.d.). Auxiliary laboratory-made devices, namely joints, grounding electrode, and tubular and reference electrode supports, were used and constructed as previously described (Alegret et al., 1987).

An Orion 90-00-02 double-junction electrode (Orion Research, MA) with a 10% KNO₃ solution was used in the outer compartment as reference electrode.

The summing of the potentials of the membranes comprised in the tubular potentiometric detector was carried out by means of a laboratory-made summing device similar to that described by Couto et al. (1997).

The gas diffusion unit consisted of one cavity in each half, 2 mm wide, 0.5 mm deep, and 7 cm linear length. In this unit, screw threads were made in each planar half to fit it in the FIA manifold. This unit comprised a poly(tetrafluoroethylene) diffusion membrane (PTFE) (plumber stripe) that was replaced whenever the results of the determinations were not reproducible.

Construction and Evaluation of the Tubular Potentiometric Detector. The iodide-sensitive potentiometric detectors were constructed as previously mentioned (Couto et al., 1997), using two homogeneous crystalline membranes 3 mm apart.

The sensor for membrane preparation consisted of a mixture (1:1) of silver iodide/silver sulfide. The membranes were prepared by pressing 0.25 g of the pulverized sensor at 19 000 kg cm⁻², producing a disk with 10 mm diameter and 0.4 mm thickness.

For detector construction (Figure 1), a rectangular silver plate (2 × 4 mm) was soldered to the inner conductor of a shielded electric cable and glued with conductive silver epoxy resin to a square membrane. After this dried, each membrane was placed in the rectangular cavity (3 × 4.5 × 7.5 mm) of a perspex cylinder and filled with a nonconductive epoxy resin. After hardening, the set was drilled (0.8 mm channel) through the center of the two membranes.

The surface of the sensor membrane was restored, whenever the slope diminished, by polishing with a damp cotton thread with aluminum oxide (Buehler 40-6603-030-016) followed by conditioning for a few hours in a 1 × 10⁻³ M potassium iodide solution.

The behavior of the iodide-sensitive tubular detectors in continuous flow was assessed by using the low-dispersion FIA system in which 0.1 M potassium nitrate with 5 × 10⁻⁶ M iodide for ionic strength adjustment and baseline stabilization was used as carrier. A 200 μL standard calibration aliquot was inserted into the carrier solution that flowed at a 8.0 mL min⁻¹ rate to the detector that was ~30 cm away from the injection valve. Under these conditions, the trials of the detector calibration in KI solutions with the ionic strength

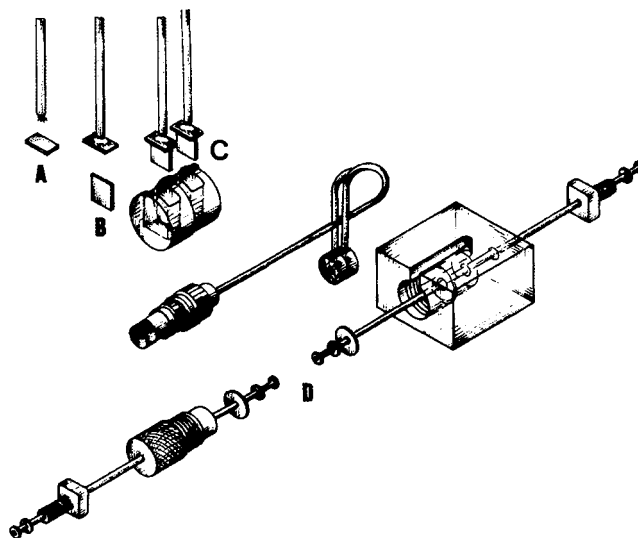


Figure 1. Plot representing the construction and assembly of the double-membrane tubular potentiometric detector sensitive to iodide: (A) the shielded cable is attached to a silver plate; (B) the membrane is glued to the silver plate with a silver-based epoxy resin; (C) the membranes are housed in a double-perspex cylinder, 3 mm apart, and a hole is drilled at the membrane center; (D) the sensor module is set in a rectangular perspex block for incorporation in the FIA system.

adjusted to 0.1 M showed that the units presented a detection limit of 2×10^{-5} M and a constant slope of 112.4 mV dec⁻¹ in the 2×10^{-5} M to 1×10^{-1} M range. The detector reproducibility within the linear response range was assessed after 16 consecutive injections of 1×10^{-4} , 5×10^{-4} , and 1×10^{-3} M iodide standard solutions. The potential drift was $\leq \pm 0.6$ mV in all cases.

The pH effect on the detector response was assessed using a system similar to that described in Alegret et al. (1985), and it showed there were no significant variations (± 4 mV) of the detector potential when the pH varied from 3 to 12 units.

Sample Preparation for FIA Determination. For the determination of free SO₂, the wine sample was inserted into the FIA system without prior treatment. The sample treatment for the determination of total SO₂ requiring the discard of combined SO₂ was carried out according to the rapid assay method suggested by OIV (1987), and therefore a volume of 10.0 mL of wine, previously alkalized with 1.6 mL of 4 M NaOH solution, was used and the pH adjusted to ~13. The sample was left still for 5 min, and afterward 2 mL of sulfuric acid 1:9 (v/v) was added, to enable pH decrease; the sample was then immediately inserted into the FIA system.

When the samples were analyzed according to the procedure officially described (OIV, 1987), the acidification required to discharge the combined SO₂ was carried out and later an excess of concentrated sulfuric acid was added.

RESULTS AND DISCUSSION

For the determination of SO₂ in wine, a FIA manifold (Figure 2), comprising a tubular potentiometric detector (TE) of increased sensitivity, a reference electrode (RE) and a gas diffusion unit, was established and optimized. The wine sample (500 μL) was inserted in a carrier (water), converging at X with a 0.4 M HNO₃ solution. The SO₂ discharged diffused through the PTFE membrane comprised in the gas diffusion unit to an acceptor channel, in which an iodine solution with a concentration of 2.5×10^{-5} or 5×10^{-5} M flowed. The variation of the iodide concentration caused by the oxidation reaction of the SO₂, after its diffusion to the acceptor channel, was monitored downstream by the potentiometric detector composed of the tubular detector.

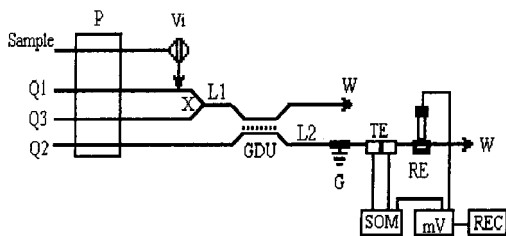


Figure 2. FIA manifold for the evaluation of SO_2 in wine: (P) peristaltic pump; (Vi) injection valve; (L_i) length (cm), $L_1 = 50$ cm and $L_2 = 35$ cm; (Q_i) flow rate (mL min^{-1}), $Q_1(\text{H}_2\text{O}) = 3.1$, $Q_2(\text{I}_2) = 4.5$, and $Q_3(\text{HNO}_3) = 2.2$; (RE) reference electrode; (TE) tubular electrode; (mV) potentiometer; (REC) recorder; (G) grounding electrode; (GDU) gas diffusion unit; (X) confluence; (SOM) summing device; (W) waste.

The manifold was then evaluated regarding the influence of the different physicochemical and hydrodynamic parameters to enable the measurements to be carried out within a wide concentration range, with a maximum of sensitivity and without prejudice of the sampling rate.

Therefore, the effect of variation of the iodine reagent concentration on the intensity of the analytical signal provided by the detector was studied by performing consecutive calibrations with standard SO_2 solutions and concentration levels between 3.2 and 180 mg L^{-1} . It was found that there was a linear increase of the analytical signal peak height, which corresponded to the trial of the solution with 90 mg L^{-1} when the iodine concentration in the acceptor solution was diminished from 5×10^{-2} to $2.5 \times 10^{-5} \text{ M}$. It was also found that for concentration levels $>5 \times 10^{-2} \text{ M}$, the presence of an excess of iodide, used in the iodine solubilization (Vogel, 1988), provided a very low peak height of the analytical signal for solutions with the lowest SO_2 concentration. For iodine concentration values $<2.5 \times 10^{-5} \text{ M}$, the potential variation of the most concentrated solutions was insignificant. The optimization of this parameter was therefore restrained both by the concentration range of SO_2 to be determined in different samples and by the potential stability of the detector baseline. Hence, a $2.5 \times 10^{-5} \text{ M}$ reagent concentration was selected for concentrations ranging from 3.2 to 22.4 mg L^{-1} . For higher values, up to 180 mg L^{-1} , an acceptor solution with an iodine concentration of $5 \times 10^{-5} \text{ M}$ was used.

The effect of the HNO_3 concentration was also assessed by adding this solution to the sample through X confluence. The studies were carried out using acid concentrations equal to 0.4, 0.04, and 0.004 M, respectively, and by submitting the standard solutions to a treatment similar to that used in the determination of total SO_2 . The values obtained showed that there was an increase of signal sensitivity when pH diminished, which corresponded to an increase of the SO_2 discharge. Hence, the 0.4 M acid concentration was selected.

The effect of HNO_3 on the breakage of the bound forms of sulfite was also evaluated. Equimolar mixtures of standard SO_2 solutions and formaldehyde were allowed to react at room temperature and pH 5–6 for the formation of hydroxymethanesulfonate (HMS). The resulting solution was injected in the proposed system either immediately or after 20 min. No analytical signals were observed, indicating that under the diffusion conditions used in the FIA system no breakage of the bound forms occurred.

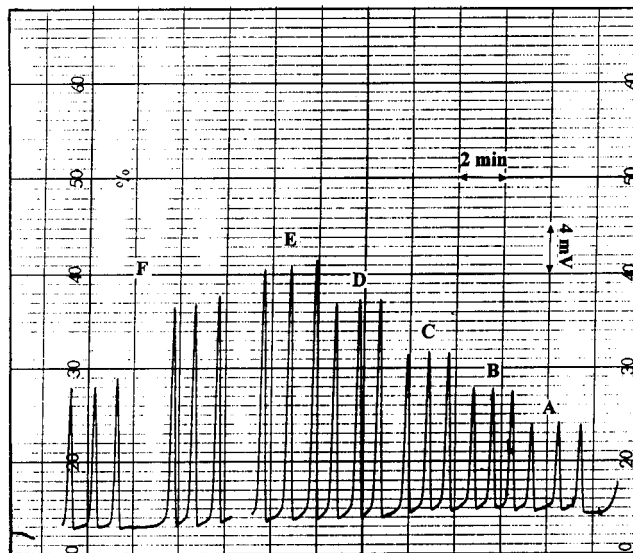


Figure 3. Recorder output corresponding to the tracing of a calibration curve and the analysis of wine samples. Concentrations injected were (A) 32.0, (B) 44.8, (C) 64.0, (D) 96.0, and (E) 128.0 mg L^{-1} ; (F) wine samples.

The influence of the injected sample volume was assessed jointly with the variation of the flow path of the gas diffusion chamber used to separate SO_2 . Therefore, injection volumes of 100, 200, 500, and $1000 \mu\text{L}$ were tested with diffusion chambers of about 3.5, 7.0, and 17.5 cm length, respectively. For a flow path of 3.5 cm it was found that, whatever the injection volume tested and for the concentration range analyzed, the calibration linearity was low because the diffusion extent was not the same at all concentration levels. Using a flow path of 17.5 cm for low injection volumes, the peak height of the analytical signals was low, especially for less concentrated solutions, due to the sample dispersion occurring in the dead volume of the diffusion chamber. Furthermore, the sampling rate was compromised. A 7 cm flow path and an injection volume of $500 \mu\text{L}$ were selected, and a good compromise among linearity, sensitivity, and sampling rate was consequently obtained. The distance between the X confluence and the gas diffusion unit was studied using flow paths of 15–115 cm length. It was found that when the length increased, the dispersion of the SO_2 discharged increased as well and, therefore, the analytical sensitivity decreased. Hence, the shortest length (~ 50 cm) was selected. The distance between the diffusion chamber and the detector was also optimized by being varied up to a maximum of 50 cm. Lengths <35 cm were not sufficient to enable the SO_2 oxidation over a considerable extent. A length of 35 cm was therefore selected as the best compromise between the progression of the oxidation reaction and the dispersion effect of the iodide formed.

The effect of the flow rate on the potentiometric detector response was evaluated between 2.0 and 5.0 mL min^{-1} both for the sample carrier channel (Q_1 and Q_3) and for the acceptor channel (Q_2). The flow rates were kept similar in both sides of the diffusing membrane, which avoided its deformation and consequently prolonged its lifetime. It was found that the response range was the highest for flow rates between 3.0 and 4.5 mL min^{-1} . When the flow rates were $<3 \text{ mL min}^{-1}$, the detector response range decreased, whereas values

Table 1. Results Obtained in the Determination of Free and Total SO₂ in 26 White Wine Samples by FIA Method (FIA) and the Rapid Assay Method (REF)^a

sample	FIA (mg L ⁻¹)	REF (mg L ⁻¹)	RD %	sample	FIA (mg L ⁻¹)	REF (mg L ⁻¹)	RD %
1	152.9 ± 1.0	148.8 ± 1.5	-2.8	14	83.4 ± 3.5	84.8 ± 4.5	1.7
2	110.7 ± 6.6	116.8 ± 2.3	5.2	15	137.3 ± 1.0	137.6 ± 1.2	0.2
3	103.2 ± 1.7	109.6 ± 1.7	5.8	16	86.4 ± 1.1	88.8 ± 4.5	2.7
4	93.8 ± 1.0	91.2 ± 1.0	-2.9	17	139.9 ± 1.0	139.2 ± 1.0	-0.5
5	106.5 ± 6.0	107.2 ± 2.3	0.6	18	116.4 ± 1.0	116.0 ± 1.2	-0.4
6	104.3 ± 3.0	107.2 ± 2.3	2.7	19	55.6 ± 1.0	54.4 ± 1.1	-2.2
7	101.9 ± 1.0	104.8 ± 1.1	2.8	20	41.6 ± 2.0	40.0 ± 2.3	-4.0
8	158.9 ± 1.0	157.6 ± 1.1	-0.9	21 ^b	40.6	38.4	-5.8
9	111.4 ± 0.5	113.6 ± 0.1	1.9	22 ^b	37.0	35.2	-5.1
10	142.8 ± 1.0	149.6 ± 1.1	4.5	23 ^b	43.6	41.6	-4.7
11	179.5 ± 1.0	177.6 ± 1.0	-1.1	24 ^b	103.1	94.4	-9.2
12	103.2 ± 1.0	103.2 ± 1.1	0	25 ^b	80.7	76.8	-5.1
13	115.9 ± 3.0	110.4 ± 4.5	-5.0	26 ^b	107.5	99.2	-8.4

^a Mean value and standard deviation of two determinations. ^b Free SO₂ determinations.

Table 2. Results Obtained in the Determination of Free and Total SO₂ in Red Wines by the Proposed FIA Method and Recovery Assays

sample	free SO ₂ (mg L ⁻¹)	total SO ₂ ^a (mg L ⁻¹)	recovery ^b (%)
1	14.2	133.9	101.6
2	13.0	69.8	98.1
3	8.9	39.7	96.1
4	5.2	51.5	98.0

^a Mean value of two determinations. ^b Recovery values of total SO₂, obtained by using the specified methodology, after addition of 0.35 mL of a 0.1 mol L⁻¹ Na₂SO₃ solution to 50 mL sample solutions.

>4.5 mL min⁻¹ caused a decrease of linearity and reproducibility of the analytical signals.

The FIA system optimized as described above enabled a maximum sampling rate of 100 samples h⁻¹ (Figure 3), when the concentration of SO₂ varied from 3.2 to 22.4 mg L⁻¹, and a maximum of 75 samples h⁻¹ for higher concentration levels up to 180 mg L⁻¹.

Analytical Applications. The present FIA manifold was applied to the determination of total and free SO₂ in 30 samples of white and red Portuguese wines of different origins (Tables 1 and 2). The quality of the results obtained with the FIA system for white wine total SO₂ (C_F) was assessed by being compared with the results provided by the rapid assay method (C_R). The linear relationship C_F = 0(±3) + 0.99 (±0.02)C_R mg L⁻¹ (R = 0.995) could be then established. Student's *t* test was also estimated, and a theoretical value of 0.863 was obtained for the determination of white wine total SO₂, less than the fixed value (2.093) for a reliable interval of 95% (McCormick and Raach, 1987). The results obtained in the determination of free SO₂ by the proposed FIA method were slightly higher than those obtained by the rapid assay method because the FIA determination was performed in a shorter period of time. Red wine total SO₂ analytical determinations were tested by recovery assays, with recovery results close to 100% (Table 2). The within-run precision of FIA methodology was assessed by calculating the relative standard deviation after processing 12 times each of two samples with 139.9 and 64 mg L⁻¹ total SO₂ concentrations, respectively. The values obtained showed a good precision, the relative standard error being <1.7%.

Conclusions. This work confirms that an automatic process of SO₂ determination in white and red wines using a FIA system with potentiometric detection, of simple construction and comprising only one gas separation procedure, can be accomplished. The proposed methodology compares well with the reference method

proposed by EC as well as with the rapid iodometric assay procedure regarding its easy handling, selectivity, and determination rate (75–100 samples h⁻¹). Potentiometric detection avoids the specific pretreatment of the samples, namely the elimination of the wine color. The use of a crystalline membrane tubular unit without inner reference solution also contributes to a physically robust FIA manifold, enabling multiparametric determinations on the same sample. Using a potentiometric detector with increased sensitivity presents the advantage of obtaining more accurate results, mainly when the contents of SO₂ are too low such as in the determination of the free SO₂.

Besides these advantages, the developed analytical method is characterized by the low consumption of reagents (about 3 mg of iodine per determination) compared to other FIA procedures used in the analysis of SO₂, which is very important for industrial control.

The results obtained in this work, as well as previous experiments performed by our group, enable us to conclude that this methodology can be applied to the analysis of other beverages, such as beer, requiring only the adjustment of the iodine solution concentration to the SO₂ content of the matrix.

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