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Determination of sulphite in wine by flow injection analysis with indirect electrochemical detection

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Abstract. A flow-injection method has been developed for the determination of total sulphite in wine samples. After hydrolysis of bound sulphite, sulphur dioxide is separated from the matrix by means of an in-line gas diffusion module. For detection indirect amperometry is used, with iodine as oxidizing reagent. The iodine can be generated in-line by merging and mixing iodate and iodide solutions, or alternatively, electrochemically from iodide. With the latter method the best results were obtained. The reproducibility of the peak heights is better than 2%. The linear range of the method can be regulated by adaptation of the current applied to generate the iodine reagent. Due to the low detection limits obtained (0.05 mg L^{-1}), wine samples can be strongly diluted before injection, which makes the sample pretreatment fast and simple. Good agreement has been found with the results obtained for the total sulphite concentration in different wine samples by titration.

Introduction

Sulphur dioxide is used as a preservative in wine to prevent oxidation and bacterial growth. In wine samples it is present partly in the free, ionized form and partly bound to other constituents such as acetaldehyde. Because of the potential toxicity of sulphite, its concentration in wines is controlled by law. In the Netherlands, maximum total sulphite levels of 160 and 210 mg L^{-1} are allowed for red and white wines, respectively. In the last years, in several countries a trend can be discerned towards the production of wines with lower sulphite concentrations [1].

The classical method to determine the total concentration of sulphite in wine and other beverages is by iodometric titration after hydrolysis of the various sulphite complexes and sometimes distillation [2, 3]. However, this is a rather time consuming procedure. To achieve a higher sample throughput, several flow-injection analysis (FIA) methods have been developed for sulphite determinations. In most successful FIA methods a gas-diffusion module is used to separate the sulphur dioxide from the acidified matrix. Detection is most often performed by spectrometry after mixing with a colour reagent, such as pararosaniline [4–7] or p-aminoazobenzene [8]. Alternatively, the decolorization of a dye such as malachite green [9, 10] can be used to monitor the diffusion of sulphur dioxide through the diffusion membrane. Other detection schemes in FIA are based on chemiluminescence [11, 12] or on enzymatic reactions [13].

Since the use of toxic or expensive reagents is not required in amperometry, this could be an attractive detection method for sulphite. However, the sensitivity and reproducibility of amperometric detection of sulphite suffer from the high overpotential required for the electrochemical oxidation [14, 15]. Fogg et al. [16] circumvented this problem by using indirect amperometry with iodine as an oxidizing reagent for sulphite. The iodine was produced in-line from iodate and iodide in a reverse FIA set-up and the excess of iodine after the reaction with sulphur dioxide was measured by amperometry in the reduction mode. The decrease of the iodine peak size was rectilinear with the sulphite concentration in the sample within a certain range.

In our laboratory indirect amperometric detection with iodine has been used in the past for the determination of sulphur compounds separated by liquid chromatography [17, 18]. In these studies the iodine was produced in-line from iodide using an electrochemical production cell between the column and the detector. In the present study we have adapted this detection scheme for the determination of total sulphite in wine samples using an FIA system with a gas-diffusion module. Different ways to add the iodine reagent have been compared. Total sulphite concentrations in wine samples obtained with the FIA method have been compared with titrimetric results.

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Experimental

Chemicals and solutions

All chemicals used were of analytical grade quality. To stabilize the sulphur dioxide, solutions were prepared in 10% (v/v) ethanol and deaerated with helium prior to use. A standard solution with a concentration of approximately 200 mg L^{-1} was prepared from sodium sulphite and titrated with iodine to determine the exact concentration. This solution was prepared fresh daily, and diluted as appropriate directly before use. Bottled wine samples were obtained on the local market. Appropriate dilution and analysis was performed immediately after opening of the bottles.

Apparatus

A Gilson (Villiers-le-Bel, France) Minipuls 2 peristaltic pump was used with polyethylene pump tubes. Other tubing was 1 mm inner diameter PTFE. Samples were injected with a Rheodyne valve with a 130 µl injection loop. The gas diffusion cell was home-made. It is constructed of two plexi-glass blocks, each with a groove of 8.0 cm length, 2 mm width and 0.2 mm depth, with a gas-permeable PTFE membrane (plumber tape) of 45 µm thickness clamped between them. Each groove has an inlet and an outlet in order to pass the donor and the acceptor streams. In the final set-up a 50 cm × 1 mm i.d. mixing coil was used between the injection valve and the diffusion module and a 20 cm × 1 mm i.d. reaction coil after the point of merging of the acceptor and iodine solutions.

The KOBRA electrochemical generation cell (Lamers and Pleuger, 's Hertogenbosch, The Netherlands) has been described elsewhere [19]. A Metrohm (Herisau, Switzerland) E 585 current source was used to supply currents of 5 or 25 µA. The Metrohm wall-jet type amperometric detector was equipped with glassy carbon working and auxiliary electrodes and a Ag/AgI reference electrode. The outlet of the detector was connected to the counter-electrode compartment of the generation cell, to sweep away reaction products of this electrode to waste. A Model 174 A potentiostat/amplifier of Princeton Applied Research (Princeton, NJ) was operated at 0.00 V for the monitoring of iodine. The signal was registered with a stripchart recorder. Measurements were performed at ambient temperature (21 ± 2 °C).

Results and discussion

Indirect detection of sulphite

As has been shown before [17, 18], iodine or triiodide can be selectively detected in flowing solutions at a working electrode potential of 0.0 V vs. Ag/AgCl. With the electrochemical detector cell as used here, a coulometric efficiency for iodine of 7.0 ± 0.5% was found at a flowrate of 1 mL/min.

An acetate buffer (0.05 mol L^{-1}, pH 4.7) was used as the carrier solution. Three systems have been tested to add iodine to the carrier solution. First, dilute triiodide solutions ($2 \cdot 10^{-5}$ to 10^{-4} mol L^{-1} iodine and 0.01 mol L^{-1} potassium iodide in 10% ethanol) were prepared and added through a second line to the carrier stream. However, the stability of these solutions was insufficient. Baseline currents observed with this system were not reproducible and showed severe drifting during the day.

In the second system tested, iodine was generated inline from iodate and iodide. In a three-line setup solutions of potassium iodate ($5 \cdot 10^{-6}$ to $5 \cdot 10^{-5}$ mol L^{-1} and 0.1 mol L^{-1} HCl in 10% ethanol) and of potassium iodide ($5 \cdot 10^{-4}$ to $5 \cdot 10^{-3}$ mol L^{-1} in 10% ethanol) were merged and mixed in a reaction coil before merging with the carrier solution. With this system, reproducible baseline currents were obtained. However, even when a long mixing coil (90 cm × 1 mm i.d.) was used at the point where the iodate and iodide solutions merged, a relatively high noise level on the baseline was found due to pump fluctuations. Although with low iodate concentrations low detection limits for sulphite could still be obtained (0.06 mg L^{-1} with 5 µmol L^{-1} iodate), the linear range of detection was limited to approximately one order of magnitude.

The third system tested was a two-line setup with electrochemical generation of iodine. A iodide solution is pumped through a generation cell, where iodine is produced by oxidation in a concentration proportional to the applied generating current. Generating currents of 5 and 25 µA were used, resulting in iodine concentrations of 0.78 and 3.9 µmol L^{-1} at a flow rate of 0.5 mL min^{-1} in this line. Stable detector baseline currents and low noise levels, both proportional to the generation current, were found. The upper limit of linearity is approximately proportional to the generating current. In Fig. 1 calibration plots for sulphite with 5 and 25 µA generation currents are shown. By changing the current, the linear range of almost 2 orders of magnitude is easily adapted to the expected sulphite concentration in a sample. After a current change the baseline stabilizes within 5 min. With the 5 µA current the detection limit (signal-to-noise ratio of 2) is 0.05 mg L^{-1}.

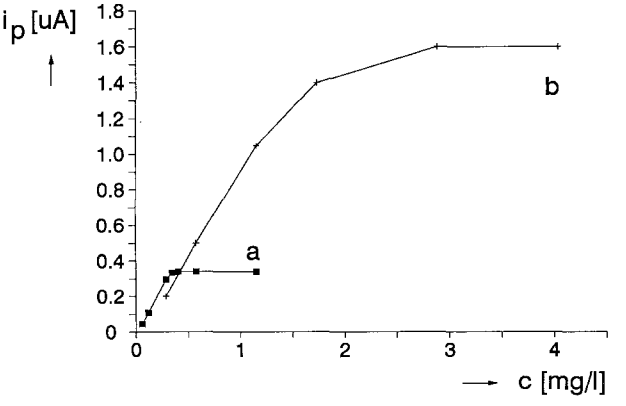

Fig. 1. Influence of the generating current on the linear range of detection: 5 µA (*a*) and 25 µA (*b*)

The gas-diffusion module

To separate sulphite from possible non-volatile interferents, a gas-diffusion module has been used. In Fig. 2 the total setup is shown schematically. Sulphite containing samples were injected into an acidic donor solution (0.1 mol L^{-1} sulphuric acid in 10% ethanol) which flows over a PTFE membrane. An acetate buffer (pH 4.7) is used as acceptor solution, flowing in the same direction on the other side of the membrane. By the choice of the pH of both solutions a selective transport of sulphur dioxide over the membrane is promoted. By comparing peak areas obtained with the gas-diffusion module with those obtained with direct injection of sulphite in the acceptor stream, it was found that the efficiency of the gas transfer into the module was 33% for concentrations between 0.5 and 2 mg L^{-1}. Although it is to be expected that with counterflow the transport process will be more efficient, this was not used. With counterflow, problems were frequently encountered with blockage of the channels and leakage of the membrane. Due to the partial recovery of sulphite and increase of the dispersion, peak heights were decreased as compared with direct injection. With a 5 µA generating current the linear range was from 0.05 to 2 mg L^{-1}. Repeated injections of a 0.9 mg L^{-1} solution showed a reproducibility of 1.6% (n = 11).

To study the selectivity of the membrane separation, solutions of other compounds capable to reduce iodine were also injected. For thiosulphate the sensitivity was only 2% of that for sulphite. With the injection of solutions of ascorbic acid up to a concentration of 0.1 mol $^{-1}$ no signals were observed. The presence of high concentrations of carbon dioxide in the sample did also not interfere in the detection of sulphite.

Wine analysis

Sulphite in wine is partly bound to other components such as acetaldehyde and anthocyanin pigments in the wines. To determine the total sulphite concentration in wine samples, the sulphite has to be liberated from its complexes before the analysis, which is promoted by dilution of the sample and acidification. Figure 3 shows the recovery of sulphite from a white wine sample diluted in different ratios with a 0.1 mol L^{-1} sulphuric acid solution in 10% ethanol. Due to the low detection limits with the proposed method, a high dilution ratio is possible. The release of sulphite in 50–100 times diluted samples could be accelerated by heating the samples in a 95 °C water bath. After 10 min the recovery was complete. Figure 4 shows recorder traces obtained with the proposed setup for standard solutions and diluted white and red wine samples. The reproducibility for repeated injections of a wine sample was 2% (n = 7). A through-put of 24 h^{-1} was achieved (single injections).

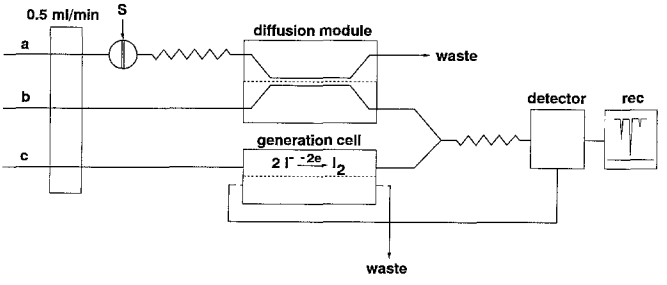

Fig. 2. Scheme of the FIA setup with the gas-diffusion module. (*a*): carrier solution, 0.1 mol L^{-1} sulphuric acid; (*b*) acceptor solution, acetate buffer pH 4.7; (*c*) prereagent, 5 mmol L^{-1} KI. All solutions contain 10% ethanol. *S*, sample (130 µl)

Table 1. Comparison of the results for wine samples obtained by the FIA method with those obtained by titration

Wine type	Origin	Sulphite concentration [mg L^{-1}][a]	
		by FIA	by titration
White	France	196 ± 3	194 ± 3
White	France	174 ± 5	178 ± 2
White	Hungary	126 ± 3	126 ± 5
Red	France	94 ± 3	91 ± 4
Red	Spain	60 ± 3	64 ± 4
Red	Bulgaria	69 ± 3	72 ± 1

[a] Mean and 95% confidence interval (n = 3)

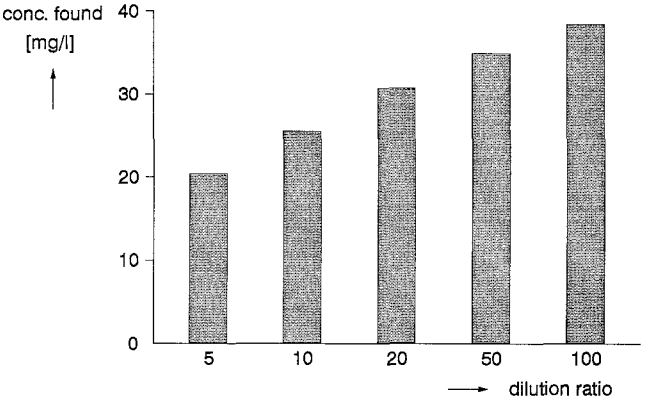

Fig. 3. Influence of the dilution ratio of a wine sample on the recovery of sulphite

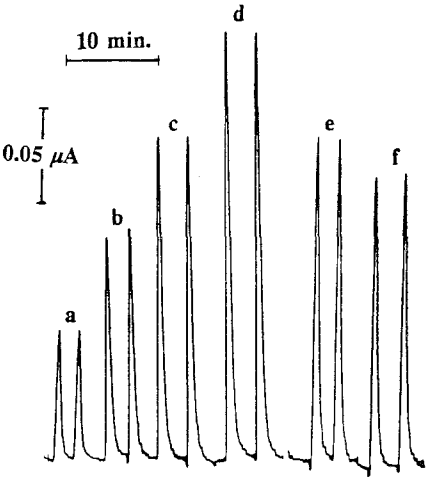

Fig. 4. FIA recorder traces obtained with duplicate injections of standard solutions of 0.9 (*a*), 1.2 (*b*), 1.5 (*c*) and 1.8 (*d*) mg L^{-1} sulphur dioxide, a white wine sample diluted 1:83 (*e*) and a red wine sample diluted 1:50 (*f*)

The results obtained with the FIA method have been compared with those obtained by the classical titration method for several bottled wines. The titration results were corrected for the contribution to iodine consumption by non-sulphite compounds. As is shown in Table 1, an excellent agreement between the two methods of analysis has been found.

References

1. Ough CS (1986) J Assoc Off Anal Chem 69:5–7
2. Ough CS, Amerine MA (1980) Methods for the analysis of musts and wines. Wiley, New York
3. Official Methods of Analysis (1984) 14th Ed., AOAC, Arlington (VA), USA
4. Beech FW, Burroughs LF, Timberlake CF, Whiting GC (1979) Bull OIV 52:1001–1022
5. Ough CS (1983) Sulfur dioxide and sulfite. In: Branen L, Davidson PM (eds) Antimicrobials in foods. Marcel Dekker, New York
6. Quattrucci E (1981) J Sci Food Agric 32:1141–1142
7. Linares P, Luque de Castro MD, Valcarcel M (1989) Anal Chim Acta 225:443–448
8. Bartroli J, Escalada M, Jiminez Jorquera C, Alonso J (1991) Anal Chem 63:2532–2535
9. Sullivan JJ, Hollingworth TA, Wekell MM, Newton RT, Larose JE (1986) J Assoc Off Anal Chem 69:542–546
10. Sullivan JJ, Hollingworth TA, Wekell MM, Meo VA, Etemad-Moghadam A, Phillips JG, Gump BH (1990) J Assoc Off Anal Chem 73:223–226
11. Burguera JL, Burguera M (1998) Anal Chim Acta 214:429–432
12. Huang YL, Kim JM, Schmid RD (1992) Anal Chim Acta 266:317–323
13. Matsumoto K, Matsubara H, Ukeda H, Osajima Y (1989) Agric Biol Chem 53:2347–2353
14. Fogg AG, Fernandez-Arciniega MA, Alonso RM (1985) Analyst 110:851
15. Granados M, Maspoch S, Blanco M (1986) Anal Chim Acta 179:445–451
16. Fogg AG, Guta CW, Chamsi AY (1987) Analyst 112:253–258
17. Kok WT, Halvax JJ, Frei RW (1986) J Chromatogr 352:27–33
18. Huang X, Kok WT (1991) J Liquid Chromatogr 14:2207–2221
19. Kok WT, Brinkman UAT, Frei RW (1984) Anal Chim Acta 162:19–32