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Fast and accurate automated method for wine SO_2 free analysis

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INTRODUCTION

Sulfur dioxide (SO_2) is used as a process control in wine making. It serves many useful functions, like in musts it acts as enzyme inhibitor preventing juice browning. As a microbiological control agent SO_2 functions not only in musts but also in wines, and it prevents the oxidation of finished wines. That's why it is added to wine during the process. Sulfur dioxide is found in wines in free forms (SO_2 and HSO_3^-) and it is also bound to compounds that incorporate a carbonyl group, such as acetaldehyde.

Total sulfur dioxide, including free and bound sulfur dioxide, is regulated and needs to be reported with a warning statement on wine labels because it is considered as an allergen. The European Union established a maximum permitted level of total SO_2 in wine varying of 150 to 500 mg/L dependent on the sugar level of the product. In the USA, the maximum level of total SO_2 is 350 mg/L (1). Both total and free SO_2 measurements can be automated using Thermo Scientific™ system reagents and discrete analyzers (2).

In this study, an automated SO_2 free method is presented. The method is based on the reaction between sulfur dioxide, p-rosaniline hydrochloride and formaldehyde. This method is designed to use optimal reagent concentration and volumes to be able to perform accurate results. The concentration of free SO_2 in the sample is calculated automatically from the calibration curve. This method enables laboratory to fully automate SO_2 analytics and replace the time consuming traditional Ripper and distillation methods.

Due to the bar-coded system reagents, this new automated SO_2 free method is very quick and easy to use. Analysis of 60 samples takes 35 minutes with only about 10 minutes for daily calibration and analyzer start-up operations. From the same samples, additionally e.g. different sugars and acids, color and total SO_2 can be run automatically. Compared to the FIA method, the photometric method requires only small volumes of reagents, thus being more economical and environmental friendly choice.

MATERIALS AND METHODS

Instruments

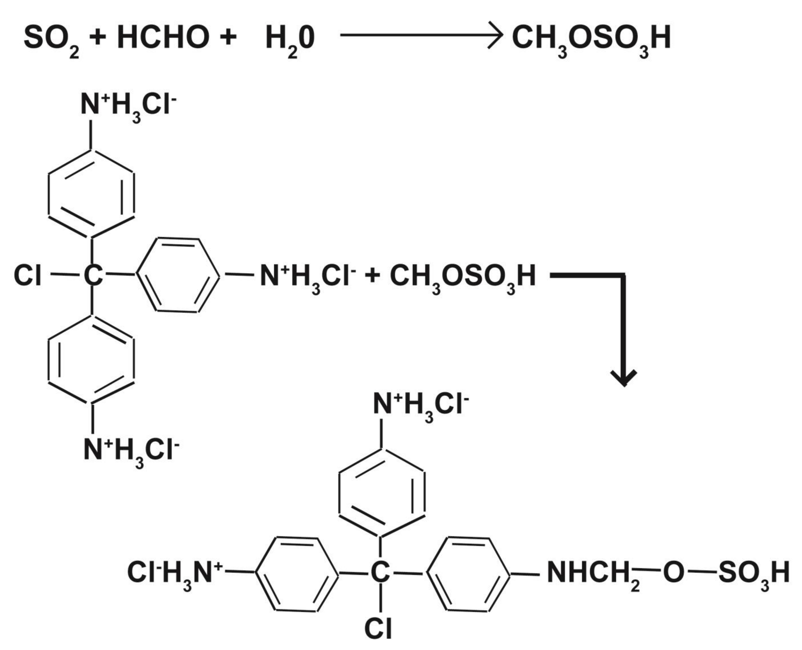
Thermo Scientific™ Gallery™ discrete photometric analyzer was used for this study.

Reference values were obtained from a FIA analyzer. Reference method was also based on p-rosaniline hydrochloride and formaldehyde reaction.

SO_2 free method principle

The method is based on the reaction between sulfur dioxide, p-rosaniline hydrochloride and formaldehyde. Method is performed at 37 ° C, using 575 nm filter and for side wavelength 700 or 750 nm filter. See Figure 1 for the reaction details.

Figure 1. SO2 free method principle



Application for wine samples

Automated SO_2 free application for Gallery analyzers consists of two reagents, end-point measurement with sample blank and 2nd order calibration curve used for result calculation. Method measuring range is from 2 to 100 mg/L and can be extended by automated dilution of the sample.

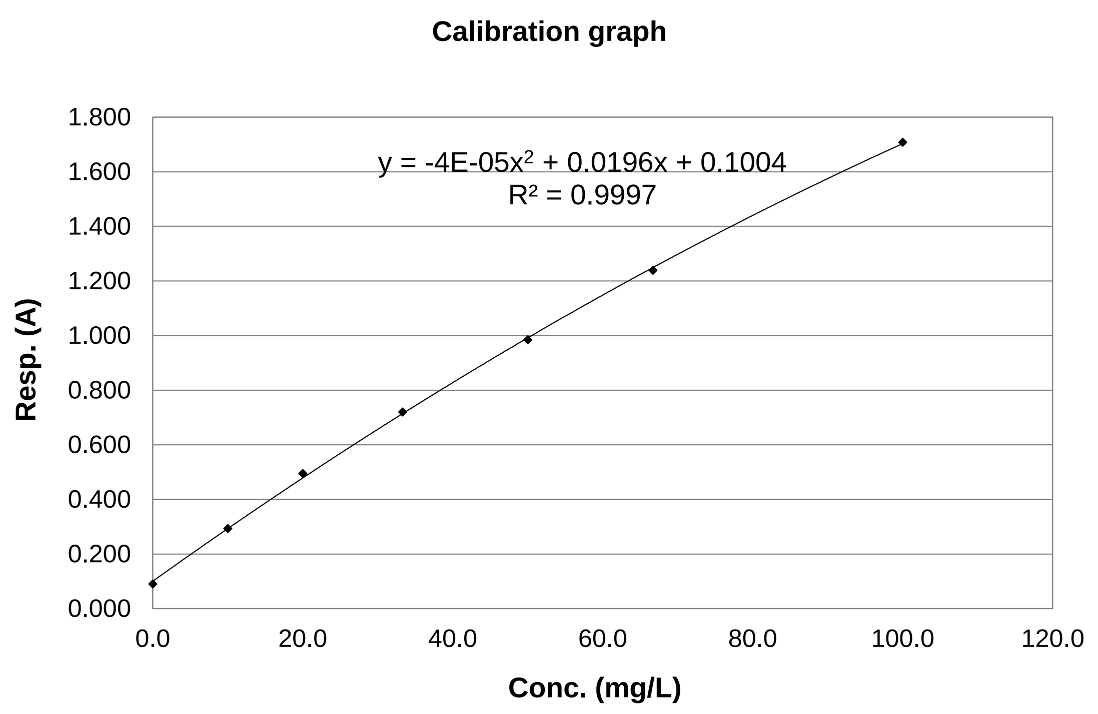
First 100 µL of SO_2 Free R1 reagent and 10 µL of sample with 10 µL of water is incubated for 30 seconds and reaction is blanked. Then 100 µL of R2 reagent is added and after 75 s incubation time the reaction is measured at 575 nm with side wavelength measurement being at 750 nm.

Reagents and calibrator

Thermo Scientific system reagent for Gallery analyzers was used. SO_2 Free–kit is available by the code number 984634.

Calibration was performed with self made standard prepared from sodium metabisulfite ($Na_2S_2O_5$ MW = 190.11 g/mol). Concentration of the standard was 200 mg/L and calibration points were automatically diluted by the analyzer (Figure 2).

Figure 2. SO2 free method calibration by using an automated dilution of the calibration stock solution



Samples

Fifty seven (57) wine laboratory samples were analyzed. Sample types were both red (N = 35) and white wines (N = 22). Reference values were determined by p-rosaniline method by a FIA analyzer. No sample pretreatment was done before the analysis.

RESULTS

From the Table 1 can be seen the correlation between the Gallery analyzer and FIA methods when they are run parallel. The concentration of SO_2 free in samples varied from 0 to 46 mg/L, average being 28 mg/L. Average of the bias was 3 mg/L when calculated from the red wine samples and it was 1 mg/L when calculated from the white wine samples.

Table 1. Bias of the two SO2 free methods is shown in the table as mg/L.

Red wine sample	Gallery (mg/L)	FIA (mg/L)	Bias (mg/L)	White wine sample	Gallery (mg/L)	FIA (mg/L)	Bias (mg/L)
Red wine 1	38	33	5	White wine 1	40	37	3
Red wine 2	1	0	1	White wine 2	43	41	2
Red wine 3	11	8	3	White wine 3	39	37	2
Red wine 4	20	16	4	White wine 4	34	34	0
Red wine 5	22	18	4	White wine 5	37	35	2
Red wine 6	26	22	4	White wine 6	34	30	4
Red wine 7	23	20	3	White wine 7	38	36	2
Red wine 8	23	19	4	White wine 8	34	32	2
Red wine 9	24	20	4	White wine 9	40	38	2
Red wine 10	31	29	2	White wine 10	37	35	2
Red wine 11	29	26	3	White wine 11	36	36	0
Red wine 12	27	26	1	White wine 12	34	35	-1
Red wine 13	37	32	5	White wine 13	34	35	-1
Red wine 14	39	36	3	White wine 14	13	12	1
Red wine 15	39	34	5	White wine 15	23	21	2
Red wine 16	36	33	3	White wine 16	0	0	0
Red wine 17	34	31	3	White wine 17	31	31	0
Red wine 18	36	33	3	White wine 18	48	46	2
Red wine 19	33	29	4	White wine 19	37	36	1
Red wine 20	31	29	2	White wine 20	39	37	2
Red wine 21	25	21	4	White wine 21	45	42	3
Red wine 22	21	19	2	White wine 22	44	42	2
Red wine 23	21	19	2				
Red wine 24	36	32	4				
Red wine 25	28	22	6				
Red wine 26	30	28	2				
Red wine 27	26	23	3				
Red wine 28	27	23	4				
Red wine 29	27	24	3				
Red wine 30	27	25	2				
Red wine 31	33	31	2				
Red wine 32	36	33	3				
Red wine 33	37	33	4				
Red wine 34	31	27	4				
Red wine 35	25	21	4				

In the Figure 3 and 4, the method correlation study is shown as a graphical presentation. The concentrations of red wine samples varied mainly from 20 to 40 mg/L and the concentrations of white wine samples from 35 to 50 mg/L.

Figure 3. Red wine sample comparison between Gallery and FIA methods

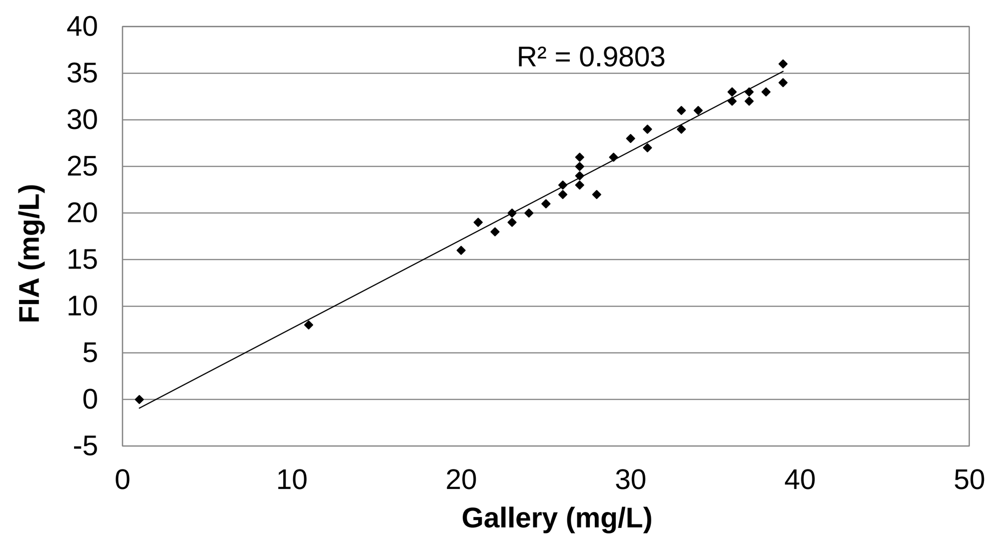
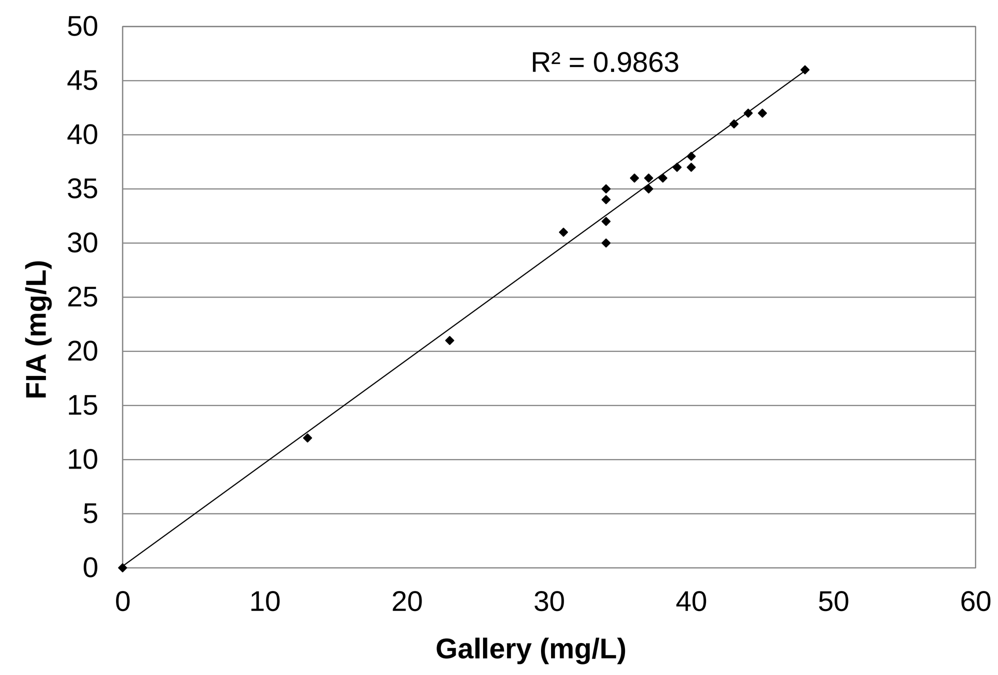


Figure 4. White wine sample comparison between Gallery and FIA methods



Both sample types showed very good correlation between the Gallery discrete analyzer and the FIA analyzer method. Also lower sample concentrations showed good correlation. Correlation coefficient was slightly better for white wines than for red wines, respectively R^2 = 0.9863 and 0.9803. All samples (N = 57) covering different types of wines showed correlation coefficient of R^2 = 0.9755. Additionally precision for one of the red wine samples (N = 40) was calculated (data not shown). Gallery method precision was 1.8 % within run, and 2.1 % between the runs.

CONCLUSIONS

The automated photometric Gallery system SO_2 free method correlates well with the FIA method. Concentration of samples varied from 0 to 46 mg/L, average being 28 mg/L. Samples (N = 57) covering different types of wines were tested with correlation R^2 being 0.9755. Precision for the red wine samples (N = 40) was 1.8% within run, and 2.1 % between the runs. This automated SO_2 free method is very quick and easy to use. Analysis of 60 samples takes only 35 minutes and enables simultaneous analysis of, e.g., different sugars and acids, color and total SO_2. Compared to the FIA method, the photometric method requires only small volumes of reagents, thus being more economical and environmental friendly choice.

REFERENCES

1. Sulphur Dioxide Content of Wines: the Role of Winemaking and Carbonyl Compounds. Jackowetz, N, Li, E and Mira de Orduña, R. Research Focus 2011-3: Cornell Viticulture and Enology

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