



Determination of Total Sulfur in Wine by Molecular Absorption Spectrometry (MAS)

Introduction

Wines naturally contain sulfites at low concentrations. Due to their antimicrobial and antioxidant properties, however, they are also added during the production process. If wine contains more than 10 mg/L SO₂, it must be labelled regarding sulfitation. Depending on the type of wine, maximum limits between 150 to 400 mg/L total SO₂ are defined, which correspond to a concentration of 75 to 200 mg/L total sulfur.

Challenge

Fast and simple determination of sulfur in wine.

Solution

Quantification of total sulfur in wine using the CS molecule bands detected with the contrAA 800.

The contrAA 800 offers the possibility to monitor these limit values for total sulfur and sulfites and can also be used in wine analysis for monitoring heavy metal and mineral content. For this purpose, the high-resolution continuum source molecular absorption spectrometry (HR-CS MAS) in combination with the fast and robust flame technique can be applied. Due to the xenon short-arc lamp as continuum light source and a high-resolution spectrometer with CCD detector, all absorption lines in the spectral range of 185 to 900 nm are available for the analysis. In addition, molecular absorption bands such as the CS band at 257.8 nm are visible and can be evaluated for the quantification of non-metals, as for quantitative determination of sulfur in this application example.

Two types of wine, a red wine and a white wine, were analyzed for their total sulfur content using the contrAA 800 flame instrument. After an oxidative pre-treatment of the samples, sulfur was quantified by CS molecule bands in the nitrous oxide flame. An aliquot of each type of wine was spiked with a defined sulfur concentration in order to observe possible analyte losses during the sample

pre-treatment or matrix effects on the signal intensity. Recovery rates near 100% demonstrate a reliable preparation and measurement procedure.

Materials and Methods

Samples and reagents

- HNO_3 (65%, p.a., Roth)
- H_2O_2 (30%, ultra trace analysis, Sigma-Aldrich)
- H_2SO_4 (96%, p.a., Merck)
- Red wine from South Africa
- White wine from New Zealand

Sample preparation

The wine samples were oxidatively treated on a heating block. For this purpose, 2 mL HNO_3 and 2 mL H_2O_2 were added to 25 mL of each wine sample. After heating for approx. 1 h at 95 °C the solutions were cooled down to room temperature and filled up in a graduated flask to 30 mL with deionized water (resulting dilution factor of 1.2). These solutions were used for the measurements.

For each sample type (red and white wine), an aliquot was spiked with a defined sulfur concentration prior to sample preparation in order to check matrix influences on the signal intensity and analyte losses.

Instrumentation

The following tables show the used device, accessory, and method settings.

Table 1: General instrument configuration and accessories

Parameter	Specification
Instrument	contrAA 800 F
Burner type	50 mm
Burner angle	0°
Scraper	Yes
Autosampler	AS-F
Injection switch	SFS 6.0

Table 2: Instrument and evaluation parameters

Parameter	Specification
Element	S
Wavelength [nm]	257.9583
Measurement time [s]	3.0
Flame type	$\text{N}_2\text{O}/\text{C}_2\text{H}_2$
Burner height [mm]	5
Fuel gas flow [L/h]	235
Base line correction	IBC-m

IBC-m: Iterative base line correction for molecule band evaluation

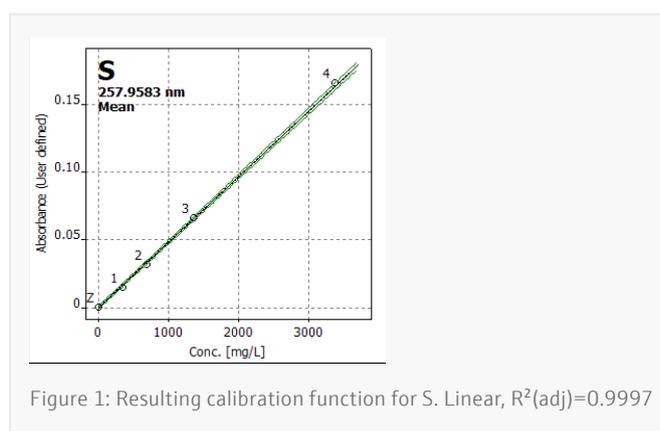
Calibration

A stock solution of 33.7 g/L sulfur was prepared gravimetrically by weighing H_2SO_4 in deionized water. The applied calibration standards were finally prepared in deionized water by dilution of this stock solution.

Table 3 shows the concentrations of the calibration standards and Figure 1 the resulting calibration function.

Table 3: Concentrations of the calibration standards

Standard	Sulfur concentration [mg/L]
Cal. std. 0	0
Cal. std. 1	337.3
Cal. std. 2	674.6
Cal. std. 3	1349
Cal. std. 4	3373

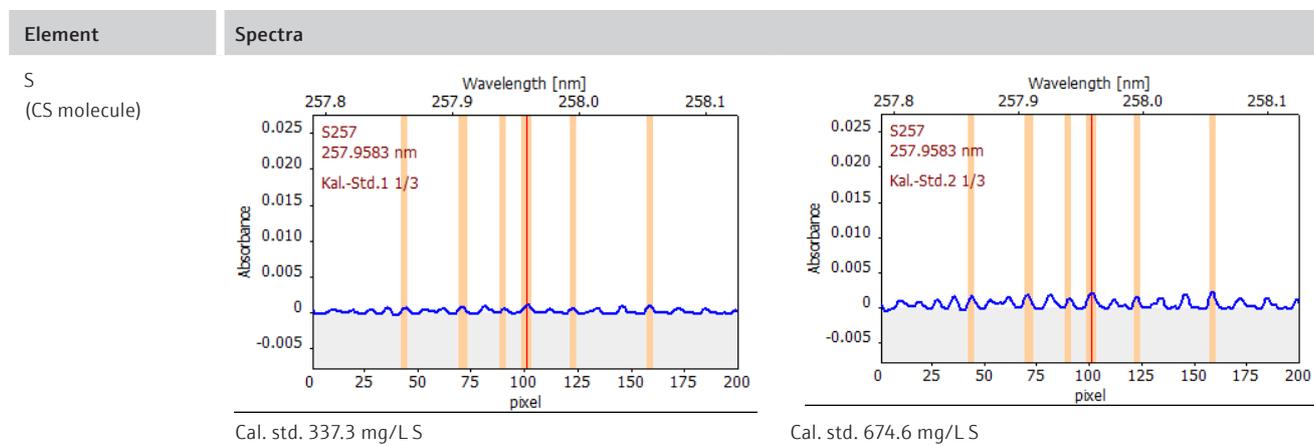


Results and Discussion

Typical spectra and spectral vicinity

Table 4 shows typical spectra of the CS molecular bands using the calibration standards as an example.

Table 4: Characteristic spectra of the evaluated CS molecule bands



Measurement results

The measurement results for the sulfur content in the analyzed wine samples as well as the converted SO₂ content are shown in Table 5. Two replicates of each sample type were prepared and measured. In order to check for a possible matrix influence on the signal intensity or an analyte loss during the sample preparation, each sample type was spiked with 674.6 mg/L sulfur. The obtained QC spike recovery rates are listed in the table as well.

Table 5: Measurement results and QC spike recovery

Sample	DF	Concentration [mg/L]		RSD _(n=3) [%]	QC spike recovery rate [%]
		S	SO ₂		
Red wine (South Africa) - 1	1.2	158.8	317.5	0.4	102
Red wine (South Africa) - 2	1.2	158.9	317.6	0.6	
White wine (New Zealand) - 1	1.2	112.2	224.3	0.7	98.5
White wine (New Zealand) - 2	1.2	119.1	238.1	2.0	

DF: manual dilution factor (by sample preparation)

RSD_(n=3): Relative standard deviation for 3 measurement replicates

Table 6 shows the limit of detection (LOD) and limit of quantification (LOQ) determined by using the blank method. The values are already corrected by the dilution factor of the sample preparation.

Table 6: Limit of detection and limit of quantification

Analyte	LOD [mg/L]	LOQ [mg/L]
S	4.3	13.0
SO ₂	8.6	26.0

LOD: Limit of detection

LOQ: Limit of quantification

Conclusion

The sulfur and sulfite concentrations in wine can be easily determined with the contrAA 800 flame technique by evaluating CS molecule bands. With the contrAA 800, all absorption lines of metals, as well as molecular absorption bands of non-metals, can be quantitatively evaluated in the spectral range of 185 to 900 nm thanks to the xenon short-arc lamp as a continuous light source, and the high-resolution spectrometer with CCD detector. In addition, the spectral background is corrected simultaneously and directly on the used wavelength. For measurements with the nitrous oxide flame, as used here for the determination of sulfur, the automatic burner head cleaner "Scraper" is recommended. It automatically removes carbon deposits from the burner slit to ensure reproducible measurement conditions. In order to observe possible analyte losses during the sample pre-treatment procedure or effects on the signal intensity caused by matrix components, each sample solution was spiked with a defined sulfur concentration. Thereby, QC spike recovery rates of 98.5 to 102% were achieved, which demonstrate the reliability of the method.

The contrAA 800 can also be used in routine analyses for monitoring the heavy metal content as well as for the determination of minerals. In combination with an autosampler, such as the AS-FD with automatic calibration and dilution function, routine applications can be additionally facilitated.

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