Direct determination of total sulfur in wine using a continuum-source atomic-absorption spectrometer and an air-acetylene flame

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Abstract Determination of sulfur in wine is an important analytical task, particularly with regard to food safety legislation, wine trade, and oenology. Hitherto existing methods for sulfur determination all have specific drawbacks, for example high cost and time consumption, poor precision or selectivity, or matrix effects. In this paper a new method, with low running costs, is introduced for direct, reliable, rapid, and accurate determination of the total sulfur content of wine samples. The method is based on measurement of the molecular absorption of carbon monosulfide (CS) in an ordinary air–acetylene flame by using a high-resolution continuum-source atomic-absorption spectrometer including a novel high-intensity short-arc xenon lamp. First results for total sulfur concentrations in different wine samples were compared with data from comparative ICP–MS measurements. Very good agreement within a few percent was obtained.

Keywords Continuum source · Atomic-absorption spectrometry · Sulfur determination · Wine analysis

Introduction

Sulfur dioxide and sulfites, which release sulfur dioxide in acidic solution, are necessary chemical additives for inhibiting undesirable bacterial growth and oxidation processes in wine production and preservation [1–8]. In terms of food safety, however, the maximum permitted amount of sulfur in wine is strictly regulated by legislation in various countries. For these reasons analysis of sulfur in wine is important in wine quality control, in which oenologists are interested in the amount of so-called "free sulfur dioxide", whereas food safety legislation is concerned with the total amount of sulfur.

Because sulfur is a non-metallic element, its determination is a persistent analytical problem. Selective methods based on direct spectrometry, for example X-ray fluorescence spectrometry [9], mass spectrometry [10], and atomic emission spectrometry [11], have been used for determination of sulfur. The instrumentation required is, however, expensive and rarely available in the laboratories of the wine industry. Two reference methods, both based on titration, are generally accepted for determination of sulfur dioxide in wine. The first is the Ripper method [12], which depends on titration with iodine using starch as the indicator. The second is the Rankine method [13] which entails removal of sulfur dioxide from the sample by flushing with air or nitrogen and oxidation with hydrogen peroxide to sulfuric acid which is finally titrated with sodium hydroxide standard solution. The reliability of the Ripper method is poor, because even wines that contain no sulfur dioxide still consume some iodine owing to reactive substances in wine, particularly in red wine [12]. In this respect the Rankine method is more advantageous. Both procedures have methodological limitations, i.e. poor precision and selectivity, and they are laborious and time-consuming [3, 7, 8]. To minimize analytical time and cost, alternative methods based on flow-injection analysis (FIA) techniques have frequently been used to process large numbers of samples. In this context, various techniques such as spectrophotometry [2, 3, 5], amperometry [4], potentiometry [6], piezoelectric sensors [14], chemiluminescence [15], and fluorescence [16] have been applied. One of the drawbacks of these concepts is the gas-diffusion step, because free sulfur dioxide can be removed from the wine neither quantitatively nor selectively by that technique [17, 18]. Therefore, a

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method that enables reliable, rapid, and inexpensive determination of sulfur in wine is still required.

Flame atomic-absorption spectrometry (FAAS) is a widely accepted technique for determination of trace metals in wine [19, 20] because of its simplicity, robustness, low cost, and high selectivity. Unfortunately, direct determination of sulfur by conventional FAAS is not possible, because the sulfur resonance lines lie in the vacuum-UV region and the element has high electronegativity, tending to form very stable molecules which are not dissociated to atoms in ordinary flames.

The first commercial high-resolution atomic-absorption spectrometer equipped with a high-intensity xenon short-arc lamp as continuum source has recently appeared (Contra 300; Analytik Jena, Germany). This event starts a new era of atomic absorption spectrometry—high-resolution continuum-source atomic-absorption spectrometry (HR-CS AAS) [21–26]. Compared with conventional atomic absorption spectrometry HR-CS AAS has many inherent advantageous features, including flexible and accurate access to any wavelength and effective and flexible background correction. Therefore, by nature, HR-CS AAS should be a suitable technique not only for atomic absorption but also for molecular absorption. Use of the latter may facilitate the determination of non-metallic elements such as phosphorus, sulfur, and halogens by using the absorption spectra of molecules, especially diatomic molecules, containing these elements [21]. In the work described here the objective was to test the feasibility of the method for wine analysis by measuring absorption spectra of carbon monosulfide (CS), produced in an ordinary air–acetylene flame. In this initial examination direct determination of "total sulfur" in wine is addressed.

Experimental

Instrumentation

All CS molecular absorption measurements were performed with a self-developed high-resolution atomic absorption spectrometer. The special features of the system are shown schematically in Fig. 1. The xenon lamp (1) (XBO 301, 300 W) was custom-made by the Gesellschaft für Lichttechnische Erzeugnisse (GLE), Berlin, Germany. Because of its specific electrode design and its high gas pressure (about 17 atm under cold conditions) the lamp operates in a hot spot mode, which leads to an increase in radiance, especially in the wavelength range below 280 nm. The radiation from the hot spot is focused by an off-axis ellipsoidal mirror (2) into a flame atomizer system (3) from a commercial Perkin–Elmer AAnalyst 800 spectrometer (Bodenseewerk Perkin–Elmer, Überlingen, Germany). A high-sensitivity module P/N N037-0393 with an aspiration rate of approximately 3.5 mL min^{-1} was used as nebulizer; this was combined with a 10-cm slit burner. The transmitted light is recorded by a double-echelle monochromator
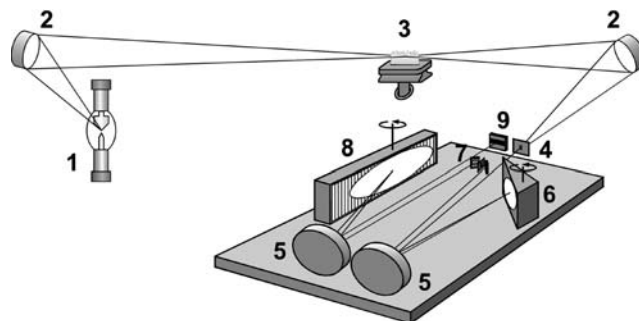

Fig. 1 Schematic diagram of the experimental arrangement used for determination of sulfur in wine samples, including a xenon lamp (1) as continuum source, a flame atomizer (3), and a high-resolution double echelle spectrometer (4–9). For details of the assembly see text

(DEMON) (4–9), developed by our group at the ISAS Berlin and described previously [22, 24]. The system has a high linear dispersion of up to $\Delta\lambda \approx \lambda/140,000$ per pixel (pixel width: 24 µm) and covers a small band of several tenths of a nanometer of the entire spectral region of analytical interest from 190 to 900 nm. The spectrometer features dynamic wavelength stabilization via spectral lines from an internal neon lamp. Wavelength accuracy is approximately 0.1 pixels (corresponding to approximately 0.15 and 0.6 pm at 200 and 800 nm, respectively). A 30° quartz prism (6) in Littrow arrangement is used in the pre-monochromator for order separation. The echelle grating (8) has 75 grooves mm^{-1} at a blaze angle of 76°. For wavelength selection both grating and prism are rotated by means of stepping motors. Signal registration is performed with a backside-illuminated CCD array (9) (192 × 64 pixels, Hamamatsu Photonics, Japan). System control and evaluation of the output signals are handled by software developed in-house.

ICP–MS measurements were made with an ELAN 6000 instrument (Perkin–Elmer, USA). Operating conditions were: RF power 1000 W; nebulizer gas flow rate 0.75 L min^{-1}; dwell time 200 ms; sweeps/reading 10.

Standards, reagents, and samples

The sulfur standard was prepared by dissolving high-purity ammonium sulfate (Fluka, Buchs, Switzerland) in deionized water. For purposes of comparison, standards prepared from sodium sulfite (Merck, Germany) were also used. Nitric acid (65%), hydrogen peroxide (30%), ethanol (99.5%), and saccharose of "pro analysi" quality were supplied by Merck. Acetylene gas was supplied by Air Liquide (Berlin, Germany). Bottled red and white wines were purchased at the local market.

CS molecular spectrum

Absorption spectra of CS produced in an air–acetylene flame were recently observed for the first time and

investigated by using a continuum source atomic-absorption spectrometer [26]. In Fig. 2, an overview spectrum of the CS absorption band system, including transition labeling by vibrational quantum numbers v, is shown. The strongest system is characterized by $\Delta v = 0$ bands. It consists of a band head located at 257.595 nm and a shoulder consisting of many sharp absorption lines corresponding to rotational transitions. The half-widths of these lines are only a few picometers and thus comparable to widths of atomic absorption lines in the same flame. Therefore, selected CS lines from this group were evaluated with regard to their application for direct determination of sulfur. The method has been proved to be very reliable and robust, because no serious spectral and matrix interferences were observed in the presence of up to 5% nitric, hydrochloric, perchloric, or hydrofluoric acids and up to 2000 mg L^{-1} solutions of Al, Ca, Co, Cr, Cu, Fe, K, Mg, Mn, Na, and Ni. Matrix interference was found only for Pb at concentrations higher than 200 mg L^{-1}, because of formation of lead sulfate as a precipitate in the solution. The LOD of the method was found to be 2.4 mg L^{-1}, the linear dynamic range covers more than three orders of magnitude.

It should, furthermore, be emphasized that the CS absorption sensitivity in an air–acetylene flame is very dependent on the chemical forms of sulfur. This is demonstrated by the measured sensitivity curves for sulfite and sulfate standards shown in Fig. 3. The standard solutions prepared from sulfite salt resulted in sensitivity three times that from sulfate salt. In principle, this may be taken as a basis for an easy method that enables determination of both "free sulfur dioxide" and "total sulfur" using a single sample solution. A detailed discussion of these effects and their consequences for speciation analysis will be given in a forthcoming paper.
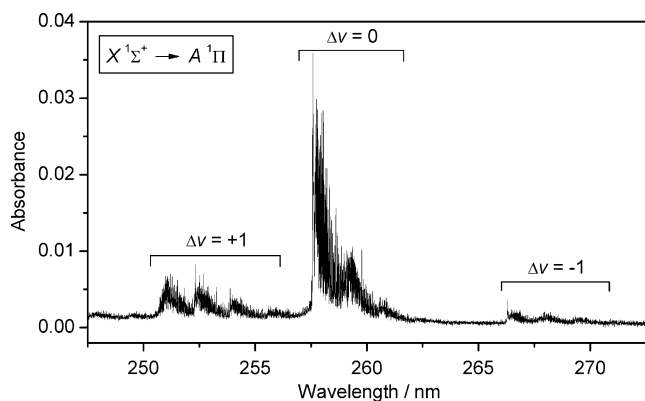

Fig. 2 Overview spectrum of the CS absorption band system recorded with the simultaneous echelle-spectrograph ARES, using an ordinary air–acetylene flame. Included is additional spectroscopic information regarding the type of electronic transition and the change of vibrational quantum number v, which characterizes the individual band system
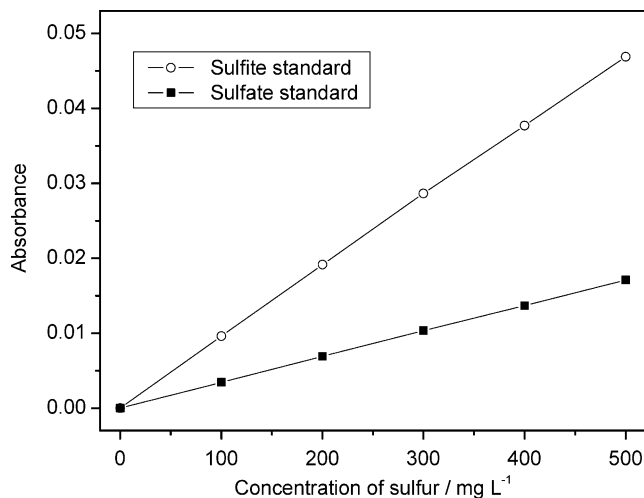

Fig. 3 Calibration curves measured at the 258.056 nm CS line using standard solutions prepared from ammonium sulfate and sodium sulfite

Procedures

As stated in a previous paper [26], CS has a relatively high bond strength of 713.4 kJ mol^{-1}, which makes it a thermodynamically very stable molecule. Unfortunately, in an ordinary air–acetylene flame CS is readily and completely consumed by reaction with atomic oxygen. Consequently, successful generation of CS spectra requires an extremely fuel-rich flame. The optimum flame composition for maximum sensitivity was found to be 3.8 L min^{-1} for acetylene and 17 L min^{-1} for air. Optimum observation height for CS absorption is in the range of 6–9 mm above the burner head. Measurements were made using the 258.056 nm CS line and a standard sulfur solution. Wavelength-integrated absorbance, i.e. the sum of the absorbance values of three pixels (a range of approximately 6 pm) around the central wavelength, was used for evaluation of the absorption signals. For background correction, three interference-free pixels on each side, corresponding to wavelengths between 258.047–258.050 nm and 258.069–258.073 nm were used. Calibration was performed using the three-point standard addition method. For this purpose, the sample solutions were spiked with 0, 50, and 100 mg L^{-1} or 0, 100, and 200 mg L^{-1} sulfur, depending on the sulfur content of the wine sample. To efficiently convert the chemical form of sulfur from sulfite to sulfate, before sample analysis 2% (v/v) hydrogen peroxide and 2% (v/v) nitric acid were added to the wine sample. Except for this procedure the red and white wine samples were analyzed by direct aspiration into the air–acetylene without any other pretreatment. The integration time per sample was 5 s.

For ICP–MS measurements it was necessary to dilute the wine samples by a factor of four. ^{34}S was used as monitored isotope. External standard solutions were prepared by diluting Titrisol sulfuric acid standard (1000 mg L^{-1}). For internal standardization ^{103}Rh was used.

Results and discussion

Wavelength selection

With regard to the principle of measurement and the standardization, the method based on the CS molecular absorption does not differ from that of ordinary flame absorption based on atomic absorption. The CS absorbance of the sample is measured and the sulfur concentration in the sample can be found by comparison with standards. Figure 4 shows a CS molecular absorption spectrum around 258 nm obtained by aspirating red wine into the air–acetylene flame. Several CS absorption lines corresponding to different rotational transitions are situated in this spectral region; these have very narrow absorption profiles with half-widths between 3 and 5 pm. The line at 258.056 nm was selected for quantifying sulfur content, because of its interference-free pixels on both sides of the absorption, which enable reliable background correction.

Method optimization

With regard to spectral and matrix effects it was found that the wine samples have the same characteristics as aqueous solutions, as mentioned in the experimental section. To gain insight into the element composition of the wine matrix, an overview measurement of a red wine sample was made by using a self-developed simultaneous spectrometer (Array Echelle Spectrograph ARES) [25]. It was ascertained that the main metallic wine components were calcium, magnesium, potassium, and sodium, all at concentrations well below 2000 mg L^{-1}. Therefore, spectral and matrix interferences caused by inorganic components in wine are not to be expected.

Because 2% (v/v) hydrogen peroxide was added to the wine samples, the effect of hydrogen peroxide on the CS absorption sensitivity had to be checked. The results are shown in Fig. 5, confirming that the signal is sufficiently independent from the concentration of hydrogen peroxide, at least up to values of 5% (v/v). Because the wine samples contained approximately 12–13% (v/v) ethanol, the effect of this on CS absorption sensitivity was also checked. From Fig. 5 it can be seen that CS absorption decreases with increasing ethanol content. In the presence of 15% (v/v) ethanol the CS absorbance decreases to 88% of its original value. Further examination revealed that the origin of the dependence could be predominately attributed to changes of the rate of aspirating of the nebulizer as ethanol was added to the solution. The rates measured were 3.4 mL min^{-1} and 2.9 mL min^{-1} for pure water and for a 10% ethanol solution, respectively. It is, therefore, not surprising that the CS absorption sensitivity is decreased. The ratio is approximately 85% and thus in good agreement with the measured value (above). Next to water and ethanol, sugar is another matrix substance in wine. Its effect on CS absorption sensitivity was also checked. No significant dependence was observed, however.

Concentration of sulfur in wine samples

The method was applied to the direct determination of total sulfur in one white wine and two red wines. The concentrations measured are given in Table 1, with comparative data obtained from ICP–MS measurements. Owing to the use of both internal and external standardization, ICP–MS can be regarded as a reliable method for determination of sulfur.
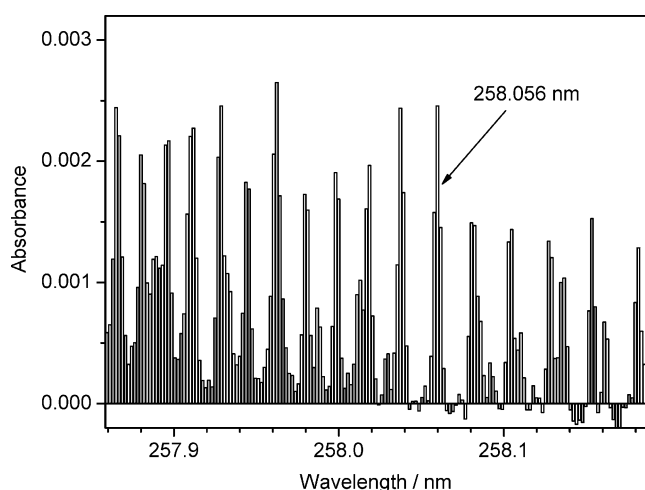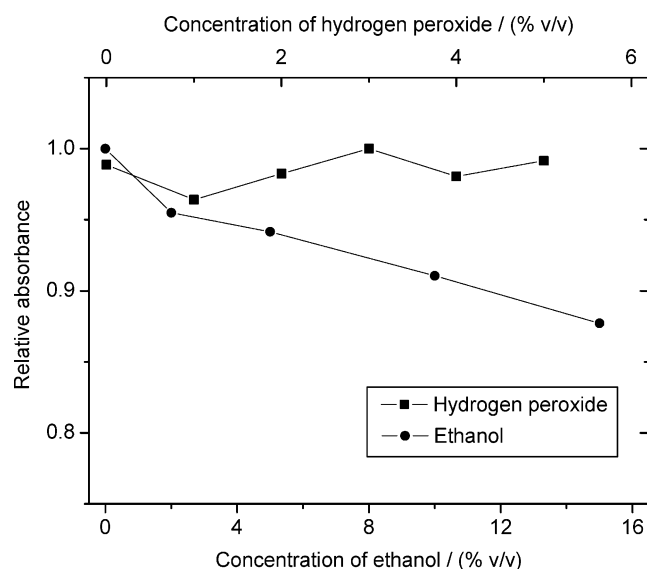

Fig. 4 Part of the molecular absorption spectrum of CS obtained from a red wine sample in an air–acetylene flame. The line at 258.056 nm was selected for quantifying the total sulfur content of the samples

Fig. 5 Dependence of relative CS absorbance at 258.056 nm on the concentration of hydrogen peroxide and ethanol in an aqueous solution of 200 mg L^{-1} sulfur

Table 1 Sulfur concentrations determined by HR-CS FAAS in white and red wine samples, and comparison with results from ICP–MS measurements

Sample	Concentration (mg L^{-1})	
	HR-CS FAAS ($n=5$)	ICP–MS ($n=5$)
White wine	113 ± 2	109.5 ± 4.4
Red wine No. 1	242 ± 3	242.7 ± 9.1
Red wine No. 2	128 ± 5	125.4 ± 4.4

All numbers in Table 1 are mean values and standard deviations based on five replicate analyses. The mean values are strikingly similar, the differences all being within the data scatter, which itself is between 1 and 4% only. These findings are evidence both of good precision and of good accuracy of the new HR-CS FAAS method.

Conclusions

The investigations described above show the feasibility of direct determination of total sulfur in wine by measuring the molecular CS absorbance with a high-resolution continuum-source atomic-absorption spectrometer, including a high-intensity short-arc xenon lamp. The accuracy of the method was verified by comparison with ICP–MS; excellent agreement, within a few percent only, was achieved. On the basis of these results, further work is planned on the analysis of sulfur in wine, with the objective of determining the specific sulfate and sulfite content by utilizing their different absorption sensitivities. This will include comparison of the results with those from the standard methods used in wine analysis. Also, more detailed examination of the effect of the concentration of alcohol and sugar in wine samples is planned. With regard to enhanced accuracy and reduced LOD, the potential of using more than one molecular line of the CS band must be investigated.

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