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Sensitive quantification of sulfur compounds in wine by headspace solid-phase microextraction technique

Yu Fang, Michael C. Qian *

Department of Food Science and Technology, 100 Wiegand Hall, Oregon State University, Corvallis, OR 97331-6602, USA

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Abstract

A sensitive solid-phase microextraction and gas chromatography-pulsed flame photometric detection technique was developed to quantify volatile sulfur compounds in wine. Eleven sulfur compounds, including hydrogen sulfide, methanethiol, ethanethiol, dimethyl sulfide, diethyl sulfide, methyl thioacetate, dimethyl disulfide, ethyl thioacetate, diethyl disulfide, dimethyl trisulfide and methionol, can be quantified simultaneously by employing three internal standards. Calibration curves were established in a synthetic wine, and linear correlation coefficients (R^2) were greater than 0.99 for all target compounds. The quantification limits for most volatile sulfur compounds were 0.5 ppb or lower, except for methionol which had a detection limit of 60 ppb. The recovery was studied in synthetic wine as well as Pinot noir, Cabernet Sauvignon, Pinot Grigio, and Chardonnay wines. Although the sulfur compounds behaved differently depending on the wine matrix, recoveries of greater than 80% were achieved for all sulfur compounds. This technique was applied to analyze volatile sulfur compounds in several commercial wine samples; methionol concentrations were found at the ppm level, while the concentrations for hydrogen sulfide, methanethiol, and methyl thioacetate were at ppb levels. Only trace amounts of disulfides and trisulfides were detected, and ethanethiol was not detected.

Keywords: Volatile sulfur compound; Quantification; Wine off-flavor; SPME; Pulsed flame photometric detection

1. Introduction

Volatile sulfur compounds are known to have very powerful and characteristic odors, and these compounds can contribute to pleasant or unpleasant aromas of a wine, according to their nature and concentration [1]. Usually when volatile sulfur compounds are present at very low concentrations, they contribute a positive impression to the wine aroma [2]. However, when present at higher concentrations, they are responsible for "reduced", "rotten egg", or "sulfury" off-flavors [3]. Balancing the two can be a significant challenge to winemakers, since many factors such as deficiencies of nutrients (amino acids and vitamins), yeast strains, metal ions, redox potential, and fermentation temperature, can all influence the formation of volatile sulfur compounds [4]. The mechanisms that form these compounds are still poorly understood, which is partially because there is no sensitive, reliable analytical method available to measure them. For this reason, it has become increasingly important to develop a quick and reliable analytical method to quantify volatile sulfur compounds in wine.

Sulfur compounds are present in trace amounts in wine, therefore a pre-concentration step is required before chromatographic analysis [5]. Solvent extraction [6,7] and static headspace extraction [8,9] have been widely used for volatile extraction, but time consumption and lack of sensitivity are the two major downfalls to limit their application for sulfur analysis in wine. In addition, some sulfur compounds are extremely volatile and chemically reactive so it is impossible to use traditional technique to enrich them.

As an alternative to traditional pre-concentration methods, solid-phase microextraction (SPME) has been successfully used to extract volatile compounds, including sulfur compounds, from the headspace of various samples [10–15]. SPME technique has been previously used to analyze volatile

* Corresponding author. Tel.: +1 541 737 9114; fax: +1 541 737 1877.
E-mail address: michael.qian@oregonstate.edu (M.C. Qian).

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sulfur compounds in wines [16–19], but quantification has not been successful due to the challenges involved with sulfur compounds as well as competitive adsorption [20]. A SPME extraction coupled with stable isotope dilution assay was successfully developed to analyze ethanethiol and diethyl disulfide in Sarah wine [21,22], but this technique is time-consuming. Moreover, not all important volatile sulfur compounds, such as hydrogen sulfide and methanethiol, could be quantified by this method.

Due to low concentrations in food, sulfur compounds are typically analyzed by gas chromatography (GC) with sulfur-specific detection, including flame photometric detection (FPD) [8,9], chemiluminescent detection (SCD) [23] and atomic emission detection (AED). Recently, pulsed flame photometric detection (PFPD) has proven to be very sensitive for sulfur compounds [15,24–26]. This technique uses a pulsed flame, rather than a continuous flame as with traditional FPD, to achieve the generation of flame chemiluminescence [27]. With PFPD, light emissions due to hydrocarbons and flame background can be ignored during each pulse of the flame by electronically gating the emission, allowing for only the sulfur portion of the spectrum to be integrated, thereby greatly increasing the selectivity and sensitivity for this detector.

In this study, a quick, sensitive method was developed to quantify the trace amounts of volatile sulfur compounds in wines by SPME and GC-PFPD. Parameters for SPME extraction were optimized to increase sensitivity, and highly reactive sulfur compounds were stabilized during the analysis. The technique was used to measure the concentrations of volatile sulfur compounds in several commercial wines.

2. Experimental

2.1. Chemicals

Sodium sulfide, methanethiol (MeSH), dimethyl disulfide (DMDS), dimethyl trisulfide (DMTS), and isopropyl disulfide (IsoProDS) were purchased from Sigma-Aldrich (St. Louis, MO, USA). Ethanethiol (EtSH), diethyl sulfide (DES), methyl thioacetate (MeSOAc), ethyl thioacetate (EtSOAc), 3-methylthiopropanol (methionol), and 4-methylthiobutanol were obtained from Johnson Mattey Catalog Company Inc. (Ward Hill, MA, USA). Ethyl methyl sulfide (EMS), dimethyl sulfide (DMS), diethyl disulfide (DEDS) were supplied by TCI America (Portland, OR, USA). Methanol and L-tartaric acid were obtained from J.T. Baker (Phillipsburg, NJ, USA), and the ethanol was from AAPER Alcohol and Chemical Co. (Shelbyville, KY, USA).

2.2. SPME extraction condition

An automatic headspace sampling system (CombiPAL autosampler equipped with a SPME adapter, from CTC Analytics, Zwingen, Switerland) with an 85 μm Carboxen-PDMS StableFlex SPME fiber (SUPELCO, Bellefonte, PA, USA) was used for extraction of sulfur compounds. Five milliliters of samples were placed in 20 mL autosampler vials. The vials were tightly capped with Teflon-faced silicone septa, and placed in an automatic headspace sampling system. The SPME conditions were set as following: samples were equilibrated at 30 °C for 30 min with 500 rpm agitation; and extracted for 15 min with 250 rpm agitation (on for 8 s, off for 2 s) at the same temperature.

2.3. Detection of volatile sulfur compound by GC-PFPD

The analyses were made on a Varian CP-3800 gas chromatography equipped with a PFPD detector (Varian, Walnut Creek, CA, USA) operating in sulfur mode. After extraction, the SPME fiber was directly injected into the GC injection port with the splitless mode at 300 °C and kept for 7 min. The separation was performed using a DB-FFAP capillary column (30 m × 0.32 mm I.D., 1 μm film thickness, from Agilent, Palo Alto, CA, USA). The oven temperature was programmed as follows: 35 °C (initial hold 3 min), ramp at 10 °C/min to 150 °C (hold for 5 min), and then ramp at 20 °C/min to 220 °C (final hold 3 min). The carrier gas was nitrogen with a constant flow rate of 2 mL/min. The temperature of the detector was 300 °C, and the detector was supplied with 14 mL/min hydrogen, 17 mL/min air 1, and 10 mL/min air 2. The detector voltage was 500 V, the gate delay for sulfur compounds was 6 ms, and the gate width is 20 ms. All sulfur compounds were identified by comparing their retention times with those of the pure standards. The sulfur responses of specific compounds were calculated by the square root of peak area.

2.4. Quantification of volatile sulfur compounds

2.4.1. Synthetic wine

The synthetic wine was made according to Mestres et al. [16] where 3.5 g L-tartaric acid was dissolved into 1 L of 12% ethanol solution, and the pH was adjusted to 3.5 with 1 M NaOH.

2.4.2. Sulfur standards and internal standard preparation

Hydrogen sulfide (H_2S) was generated by adding sodium sulfide solution into synthetic wine. Different concentrations of sodium sulfide solutions were made by dissolving the salt in distilled water (pH 7). The solutions were stored at 4 °C. Before analysis, the sodium sulfide solutions were directly added into sample vials containing synthetic wines (pH 3.5). The concentrations of H_2S were calculated based on the amounts of sodium sulfide added into the synthetic wines. The MeSH standard was prepared by bubbling pure MeSH gas directly into cooled methanol (−15 °C). Its concentration was calculated by weight. Standard solutions of 2000 ppm (w/w) of DMS, DMDS, DMTS, EtSH, DES, DEDS, MeSOAc, EtSOAc and methionol were individually

prepared in cooled methanol (−15 °C) and stored at −15 °C. Dilutions were made with cooled methanol at the same temperature.

An internal standard solution was made by dissolving 500 ppb (w/w) of EMS, 2 ppb (w/w) of IsoProDS, and 100 ppm (w/w) of 4-methylthiobutanol in methanol with 1% of acetaldehyde, and stored at −15 °C.

2.4.3. Suppression the interference of SO_2 with acetaldehyde

To eliminate the interference of SO_2 on the sulfur analysis, acetaldehyde was added into the wine to suppress the interference of SO_2. The impact of acetaldehyde on the extraction of volatile sulfur compounds was investigated. Five milliliters of wine samples with and without 200 ppm of acetaldehyde were prepared. The samples were equilibrated at 30 °C for 30 min with 500 rpm agitation, and the sulfur compounds were extracted with SPME fiber for 15 min with 250 rpm agitation and analyzed by GC-PFPD.

2.4.4. Investigation of SPME fiber selectivity to sulfur compounds

The target sulfur compounds were dissolved in methanol (each compound at a concentration of 3.4 ppm) and 0.5 μL of sample was directly injected into GC-PFPD (split ratio 1:10) to determine the detector sulfur responses for different compounds. Another mixture of target compounds (each at 136 ppb in synthetic wine) was put into a 20 mL vial, and the sample was equilibrated at 30 °C for 45 min with stirring. The headspace (10 μL) was directly injected into GC-PFPD with the splitless mode. Moreover, a mixture of sulfur compounds (1.36 ppb of each in synthetic wine) was analyzed by the SPME technique (pre-equilibrated for 30 min and extracted for 15 min at 30 °C). The GC-PFPD conditions were the same as described previously. The response of MeSH was assigned to be 1, and was used as a reference against which other sulfur compounds were calibrated. The ratio of sulfur responses of static headspace injection with those of solvent injection represented the volatility of sulfur compounds in synthetic wine under experimental condition. The selectivity of SPME fiber was calculated by comparing sulfur responses in SPME analysis with those in static headspace.

2.4.5. Calibration of standard curves

Five milliliters of synthetic wine containing different concentrations of sulfur standards and 100 μL of internal standard solutions were placed in 20 mL autosampler vials. The vials were tightly capped with Teflon-faced silicone septa, and placed in an automatic headspace sampling system. The SPME conditions and GC-PFPD conditions were set as described previously. The standard curve for individual sulfur compounds was built up by plotting the sulfur response ratio of target compound and its internal standard against the concentration ratio.

2.4.6. Calculation of recovery rates

The recovery rates of sulfur compounds were evaluated in synthetic wine as well as in Pinot noir, Cabernet Sauvignon, Pinot Grigio, and Chardonnay wines. Known amounts of sulfur compounds were added to these wines separately. The concentrations of the sulfur compounds in these wines before and after the sulfur addition were quantified by the procedure described previously. The recovery rate was calculated by the following equation:

$$\text{Recovery rate} = \frac{\text{Detected amount after addition} - \text{Detected amount before addtion}}{\text{Added amount}} \times 100\%$$

2.5. Wine analysis

Seven different commercial white wine samples (five varieties) and seven red wine samples (three varieties) from California, Oregon and Canada were obtained from market place. All wine samples were stored at 4 °C before analysis. Five milliliters of wine sample and 100 μL of internal standard solution were placed in 20 mL autosampler vials. The vials were tightly capped with Teflon-faced silicone septa. The sample vials were placed in the automatic headspace sampling system and the same SPME fiber as that used in the calibration curve was used. The SPME and GC-PFPD conditions were set as mentioned above. Triplicate analysis was performed on all samples.

3. Results and discussion

3.1. SPME extraction of volatile sulfur compounds in wine

High reactivity and low concentration are two of the biggest challenges for volatile sulfur analysis in wine. A lot of work has been done to evaluate different SPME fibers for sulfur extraction, and the results show that the fiber coated with a bi-layer of Carboxen and PDMS (polydimethylsiloxane) has high sensitivity for volatile sulfur compounds [16,18,28]. This fiber can extract highly volatile compounds such as H_2S and DMS, which cannot be easily recovered by solvent extraction or purge-trap methods.

However, some limitations have been observed with this fiber concerning the decomposition or reaction of analytes during sample preparation and GC injection, such as oxidation of DMS to dimethyl sulfoxide [11] and generation of DMDS from MeSH [15]. We found that the artifact formation of MeSH was also related to sample matrix. MeSH is even unstable in methanol and can be easily oxidized to DMDS. This oxidation was much more severe in phosphate buffer than in water. Therefore, the stabil-

ity of target sulfur compounds was a major concern in our study.

In order to stabilize sulfur compounds during analysis, it was found that pre-treatment of the instrument was required. In this experiment, the GC injection port was deactivated with BSTFA (bis(trimethylsilyl)-trifluoroacetamide), and the sample vials were flushed with inert gas. Since MeSH is not stable and the commercial MeSH solution contained detected

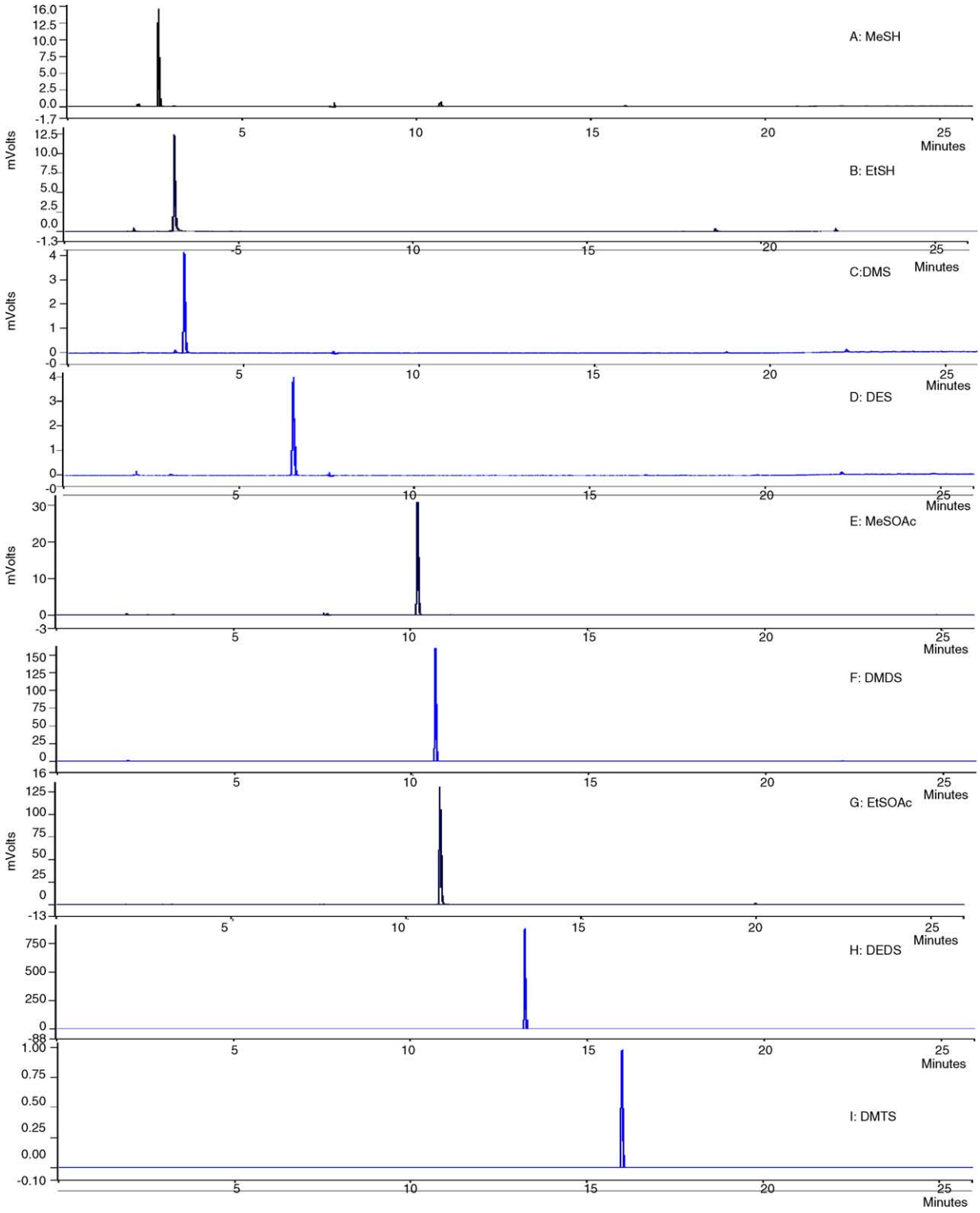

Fig. 1. The artifacts determination of sulfur compounds under SPME extraction condition in this study.

amount of DMDS, MeSH gas was used to prepare the standard solution. All the sulfur standards were freshly prepared and dissolved in a synthetic wine matrix containing 0.35% tartaric acid and 12% ethanol. In addition, the extraction temperature was kept low. When sulfur standards were checked individually only single peak was detected (Fig. 1), which indicated that artifact formation was prevented under the experimental conditions.

Headspace SPME extraction efficiency is based on the equilibrium of analytes among the three phases: the coated fiber, the headspace and the sample solution. Depending on how fast the analytes go to the headspace and are adsorbed by the fiber, the length of extraction time and temperature will be critical for SPME extraction efficiency. Generally, longer extraction time and high temperature benefited the equilibrium and increased the responses of less volatile analytes. However, because the Carboxen-PDMS fiber only has a limited number of adsorption sites, and higher molecular weight compounds (less volatile) can displace lower molecular weight compounds as a consequence of

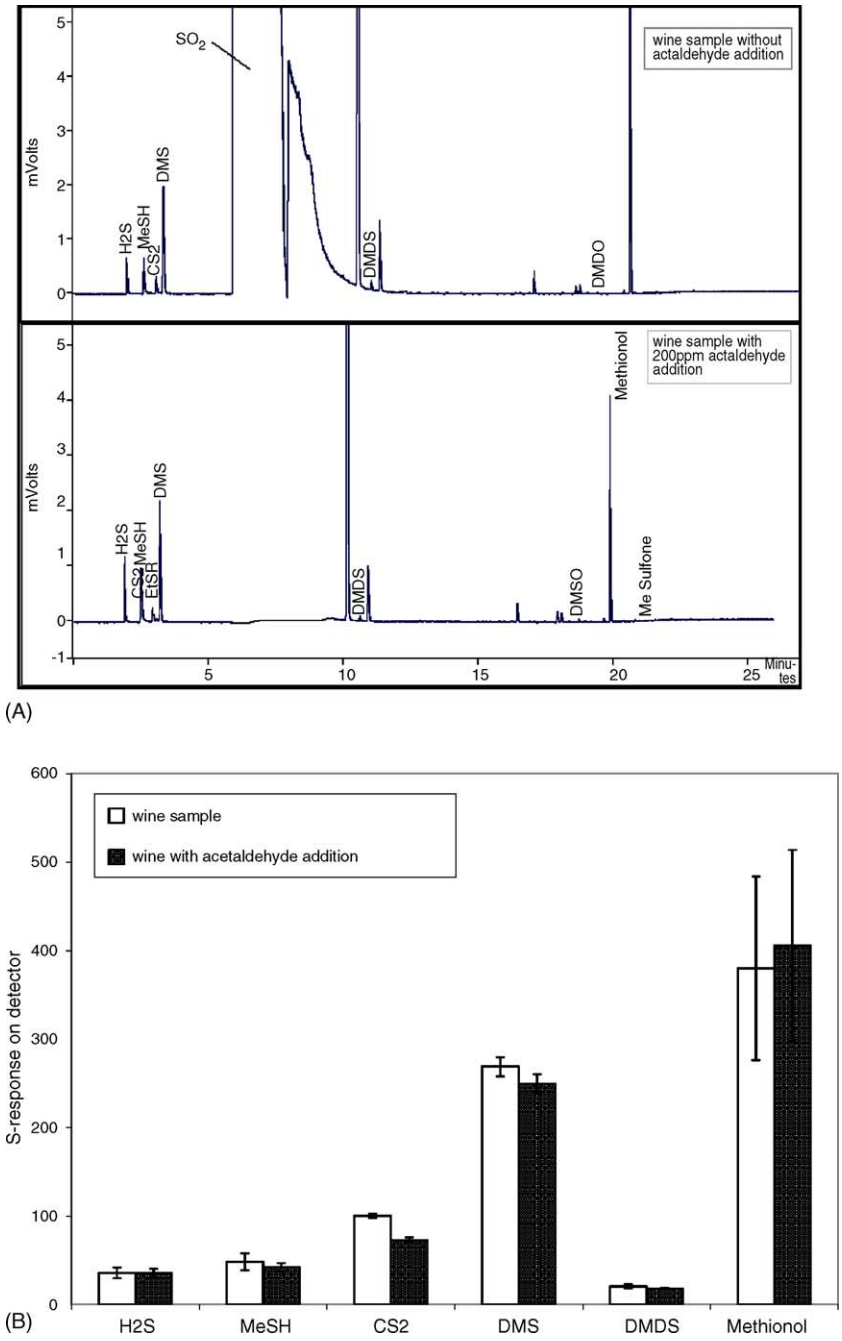

Fig. 2. (A) Chromatogram showing the effect of acetaldehyde addition on SO_2; (B) the effects of acetaldehyde addition on the extraction of volatile sulfur compounds ($n = 3$).

competition for active sites on the fiber [20], the quantification can only be achieved under non-equilibrium conditions using short extraction time, particularly for complex matrices [5,29,30]. In addition, it was noticed that more water was adsorbed by SPME fiber at above 40 °C, causing baseline shift in the chromatogram. Therefore, a short extraction time (15 min) and a low temperature (30 °C) were chosen in our study.

3.2. Quantification of volatile sulfur compounds

Quantification of volatile sulfur compounds thus far has had minimum success due to the difficulties involved in the analysis. Sulfur dioxide can be added to wine as an antioxidant and anti-microbial agent. Commercial wines can contain up to 50 ppm free SO_2 or more. The high PFPD response for SO_2 interferes with the detection of other volatile sulfur compounds, which occur in wine at significantly lower concentrations. Since SO_2 reacts with carbonyl compounds, acetaldehyde (200 ppm) was added to the wines to eliminate the interference of SO_2. As shown in Fig. 2(A), the addition of acetaldehyde can efficiently eliminate free SO_2. Moreover, addition of acetaldehyde had no effect on the measurement of other volatile sulfur compounds (Fig. 2B).

It is well known that SPME fibers have different selectivity for different compounds. The selectivity of Carboxen-PDMS fiber towards different volatile sulfur compounds in wine was investigated. As shown in Table 1, the fiber selectively extracted much more disulfides and trisulfides than DMS, EtSH and MeSH, which resulted in much higher detection sensitivity for disulfides and trisulfides. Therefore, trace amount of contaminating disulfides and trisulfides in other sulfur standards can generate very large signal. Since the concentrations for disulfides and trisulfides were very low in the experimental wine samples, the high purity of sulfur standards was critical for successfully quantification. Since the selectivity was very different among different sulfur compounds, it would be inaccurate to quantify all sulfur compounds based on only one internal standard. In this study, multiple internal standards were used to quantify different types of sulfur compounds.

Table 1
Volatility of sulfur compounds in synthetic wine and selectivity of SPME Carboxen-PDMS fiber (presented based on MeSH as 1) ($n = 3$)

	Volatility in synthetic wine	Selectivity of SPME fiber
MeSH	1.00	1.00
EtSH	0.93	0.93
DMS	0.61	1.14
DES	0.65	4.32
MeSOAc	0.19	5.21
DMDS	0.65	6.36
EtSOAc	0.31	7.39
DEDS	0.79	13.96
DMTS	0.49	14.84
Methionol	0.18	–[a]

[a] The selectivity of methionol cannot be detected based on this experiment.

To build up the calibration curves, different concentration of target compounds as well as internal standards were spiked in synthetic wine, and analyzed by SPME-GC-PFPD (Fig. 3). MeSH, EtSH, H_2S, DMS, DES, MeSOAc, and EtSOAc were calculated with EMS as the internal standard. For most of these sulfur compounds, linear responses were obtained up to a quantification limit of 0.5 ppb with the correlation coefficient (R^2) greater than 0.99 (Fig. 4A and B) and the relative standard deviations (RSD) were less than 10%. For H_2S, a quantification limit of 1 ppb and a relative standard deviation of 15% were achieved even though it is extremely volatile. IsoProDS has a similar response to that of poly-sulfides, so it was used to quantify DMDS, DEDS and DMTS (Fig. 4C). For these compounds, the quantification limits could go as low as 0.01 ppb (R^2 of the linear relationship >0.99, RSD < 10%). Methionol was calculated based on 4-(methylthio)butanol as the internal standard (Fig. 4D), and the detection limit was 60 ppb (R^2 of the linear relationship = 0.98). Although methionol responses varied a lot based on the time after the sample was prepared, its RSD value could be reduced to below 20% by internal standard correction.

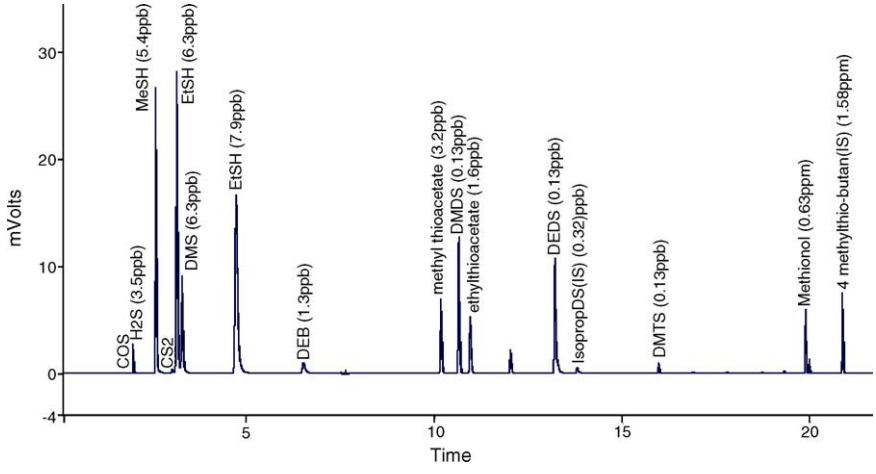

Fig. 3. Chromatogram of volatile sulfur compounds and internal standards in synthetic wine by SPME-GC-PFPD.

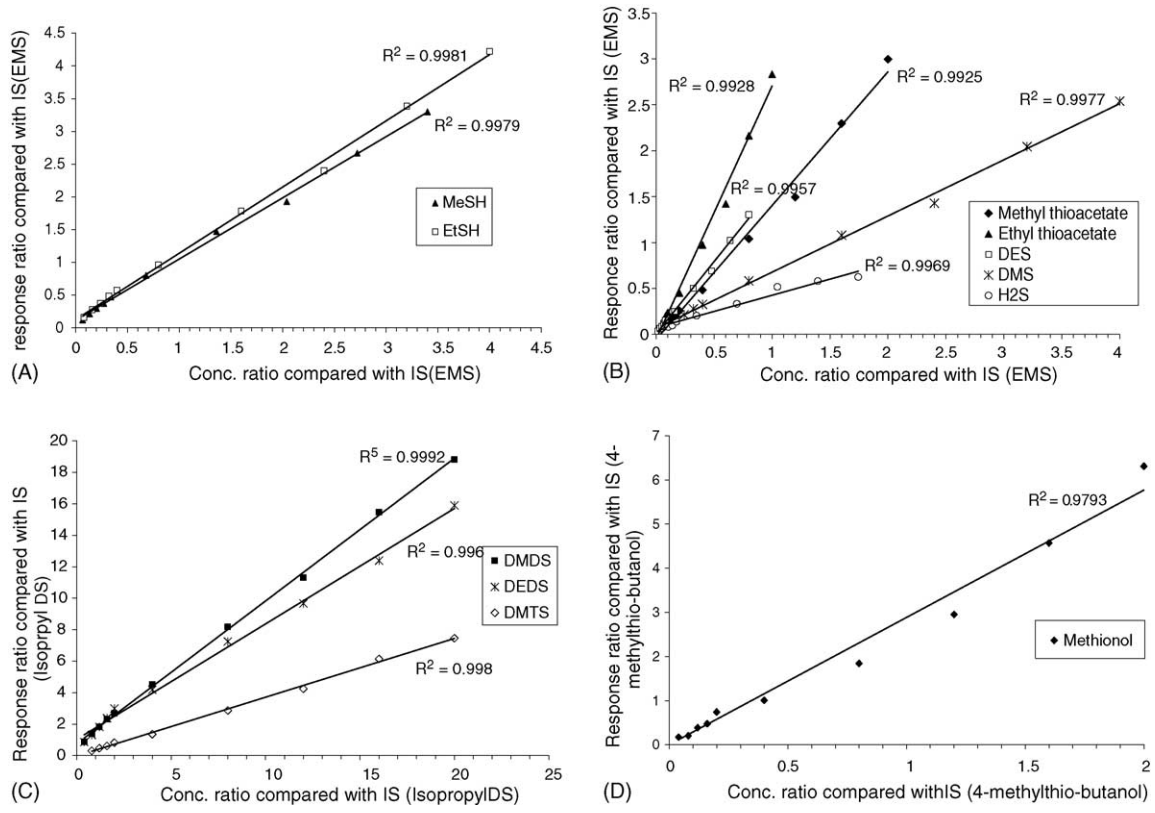

Fig. 4. Calibration curves for (A) MeSH and EtSH; (B) H_2S, DMS, DES, MeSOAC and EtSOAc; (C) DMS, DES and DMTS and (D) methionol.

To investigate the influence of the wine matrix on the recovery of volatile sulfur compounds, known amounts of target compounds (1.74 ppb of H_2S, 2.69 ppb of MeSH, 3.16 ppb of EtSH, 3.16 ppb of DMS, 0.63 ppb of DES, 1.58 ppb of MeSOAc, 0.79 ppb of EtSOAc, 63.3 ppt of DMDS, 63.3 ppt of DEDS, 63.3 ppt of DMTS, and 0.32 ppm of methionol) were added to five different types of wines. The concentrations were measured before and after the spiking of sulfur compounds. Table 2 shows the recovery rates of target compounds in synthetic wine, Pinot noir, Cabernet Sauvignon, Pinot Grigio, and Chardonnay. The recovery rates in the synthetic wine were all close to 100%. For real wine samples, the matrix did show a different effect on the recovery. However, most recovery rates fit into the range of 80–120%, which is within the analytical error. Thus this method is reliable to quantify the amount of sulfur compounds in different wines.

3.3. Sulfur analysis of commercial wines

Several red and white wines purchased in the market were analyzed

by this method, and the results were shown in Tables 3 and 4. For these commercial wines, no sulfur off-flavor problem was detected by a preliminary sensory evaluation. EtSH and DEDS were not detected in either white or red

Table 2
Recovery rates of sulfur compounds in different wine matrices (presented as 100%, $n = 3$)

	Synthetic wine	Pinot noir	Cabernet Sauvignon	Pinot Grigio	Chardonnay
H_2S	100	89	99	80	98
MeSH	99	83	93	117	117
EtSH	101	104	110	117	125
DMS	101	111	116	94	86
DES	100	98	106	108	96
MeSOAc	98	121	103	87	85
DMDS	100	107	104	108	96
EtSOAc	101	117	93	98	81
DEDS	98	84	95	110	117
DMTS	101	90	96	109	114
Methionol	101	82	106	90	120

Table 3
The concentration of volatile sulfur compounds in commercial white wine samples ($n = 3$)

Sulfur compound	Wine sample						
	Wine A Pinot Grigio from California	Wine B Pinot Grigio from Canada	Wine C Pinot Gris, from Oregon	Wine D Pinot Blanc from Oregon	Wine E Chardonnay from California	Wine F Chardonnay from California	Wine G Chardonnay From Oregon
H_2S (ppb)	4.60 ± 1.20	1.66 ± 0.49	7.89 ± 1.32	9.03 ± 1.60	1.45 ± 0.58	2.14 ± 0.43	3.59 ± 0.39
MeSH (ppb)	4.88 ± 0.37	1.09 ± 0.32	4.28 ± 0.77	2.94 ± 0.29	1.02 ± 0.40	0.48 ± 0.11	1.64 ± 0.14
EtSH (ppb)	nd	nd	nd	nd	nd	nd	nd
DMS (ppb)	17.00 ± 1.03	35.37 ± 2.15	18.08 ± 0.84	12.05 ± 0.25	27.38 ± 1.13	52.60 ± 1.54	31.57 ± 1.20
DES (ppb)	nd	nd	nd	0.27 ± 0.05	nd	nd	nd
MeSOAc (ppb)	1.68 ± 0.11	0.32 ± 0.00	1.55 ± 0.29	3.50 ± 0.82	2.18 ± 0.10	1.42 ± 0.06	1.60 ± 0.06
EtSOAc (ppb)	0.17 ± 0.00	1.00 ± 0.19	20 ± 6	22 ± 6	0.51 ± 0.03	0.58 ± 0.04	11 ± 0
DMDS (ppt)	19 ± 1	70 ± 10	0.34 ± 0.02	0.64 ± 0.20	65 ± 7	24 ± 2	nd
DEDS (ppt)	nd	nd	nd	nd	nd	nd	nd
DMTS (ppt)	18 ± 2	55 ± 6	nd	nd	111 ± 29	35 ± 6	11 ± 1
Methionol (ppm)	0.41 ± 0.14	0.22 ± 0.06	0.75 ± 0.02	0.83 ± 0.04	0.43 ± 0.11	0.47 ± 0.13	0.67 ± 0.10

nd: Not detected.

Table 4
The concentration of volatile sulfur compounds in commercial red wine samples ($n = 3$)

Sulfur compound	Wine sample						
	Wine H Gamay noir from Oregon	Wine I Cabernet Sauvignon from California	Wine J Cabernet Sauvignon from California	Wine K Pinot noir from Oregon	Wine L Pinot noir from Oregon	Wine M Pinot noir from Oregon	Wine N Pinot noir from California
H_2S (ppb)	2.68 ± 0.12	5.41 ± 1.74	7.64 ± 2.69	2.11 ± 0.41	4.70 ± 1.62	2.60 ± 0.71	9.26 ± 2.36
MeSH (ppb)	0.95 ± 0.01	1.26 ± 0.08	2.41 ± 0.24	1.56 ± 0.20	2.17 ± 0.35	1.19 ± 0.03	2.92 ± 0.29
EtSH (ppb)	nd	nd	nd	nd	nd	nd	nd
DMS (ppb)	9.34 ± 0.86	45.54 ± 0.60	67.53 ± 4.97	26.41 ± 4.03	13.58 ± 0.48	14.44 ± 0.08	11.90 ± 0.14
DES (ppb)	0.28 ± 0.04	nd	0.49 ± 0.06	nd	nd	0.34 ± 0.03	0.35 ± 0.07
MeSOAc (ppb)	2.74 ± 0.08	7.51 ± 0.07	6.83 ± 0.46	1.59 ± 0.15	1.50 ± 0.03	9.21 ± 0.28	4.10 ± 0.10
EtSOAc (ppb)	nd	0.70 ± 0.01	0.99 ± 0.06	10 ± 1	0.35 ± 0.01	13 ± 1	0.46 ± 0.04
DMDS (ppt)	0.17 ± 0.00	13 ± 1	13 ± 2	nd	31 ± 9	1.23 ± 0.04	36 ± 7
DEDS (ppt)	nd	nd	nd	nd	nd	nd	nd
DMTS (ppt)	nd	nd	nd	nd	nd	nd	21 ± 6
Methionol (ppm)	1.06 ± 0.03	1.73 ± 0.35	2.06 ± 0.24	1.13 ± 0.26	1.50 ± 0.15	1.97 ± 0.32	1.83 ± 0.41

nd: Not detected.

wines. Concentrations of H_2S and MeSH in all tested wines were found to be ranging from 0.48 to 9.26 ppb. Although previous research reported that the concentration of MeSH as low as 1.5 ppb could cause the occurrence of off-flavors in wine [23], the MeSH in our study did not cause any sulfur off-flavor problems even at concentration as high as 4.88 ppb, which may be due to its different threshold in different wines. Only a trace amount of disulfide and trisulfide were found in some wine samples. The results for methionol showed that its concentration was generally lower in white wine than in red wine.

4. Conclusion

A sensitive SPME-GC-PFPD technique was developed to analyze volatile sulfur compounds in wines. This method can be applied for detection and quantification of H_2S, MeSH, EtSH, DMS, DES, MeSOAc, DMDS, EtSOAc, DEDS, DMTS, and methionol in both red and white wines. The quantification limits can be as low as 0.5 ppb for most volatile sulfur compounds, and 0.01 ppb for disulfide and trisulfide, which are well below sensory detection limits. The development of this method makes it possible to reliably study the sulfur aroma compounds in wine.

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