

# The quantitative determination and some values of dimethyl sulphide in white table wines

by

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## Die quantitative Bestimmung von Dimethylsulfid in weißen Tafelweinen sowie einige Angaben über seine Konzentration

**Zusammenfassung.** — Für die quantitative Bestimmung von Dimethylsulfid (DMS) in Wein wurde unter Verwendung der „headspace“-Technik und von Dichlormethan als Standard eine gaschromatographische Methode entwickelt. Die Genauigkeit der Methode liegt bei einer Standardabweichung von 6%.

Bei der Anwendung der Methode auf eine Reihe von Weißweinen wurden DMS-Werte zwischen 0 und über 400  $\mu\text{g/l}$  ermittelt. DMS scheint sich während der Ausreifung des Weines in der Flasche zu entwickeln und könnte zum sogenannten Lagerungsbukett beitragen. Besonders hohe DMS-Konzentrationen wurden in älteren Riesling-Weinen festgestellt.

### Introduction

In earlier work dimethyl sulphide (DMS) was identified in white wines as a contributor to bouquet (DU PLESSIS and LOUBSER 1974). The flavour and odour threshold values of DMS in distilled water has been reported to be from 12 to 0.33 ppb (PATTON *et al.* 1956, GUADAGNI *et al.* 1963, TOAN *et al.* 1965). With these very low threshold values it is likely that DMS may be important in the consumer acceptance of wines.

Since DMS was first reported in beer by AHRENST-LARSEN and HANSEN (1964), several methods for its quantitative determinations have been reported (JENNINGS *et al.* 1972, LINDSAY *et al.* 1972). These methods were based on initial entrainment and extraction procedures and, apart from being time-consuming, were more suited for determining the higher molecular weight volatiles in beer. A method better suited for this field of study appeared to be the headspace sampling procedure (SINCLAIR *et al.* 1969, 1970).

Since DMS has been shown to contribute to wine bouquet, an analytical procedure for its quantitative determination was an essential step in further studies. The methods used for beer analysis were found to be incompatible with wines, giving unsatisfactory results. Consequently a quantitative method which was suitable for wines was developed.

### Materials and Methods

#### 1. Gas chromatography

A gas chromatograph with dual flame ionization detectors was used (SINCLAIR *et al.* 1969, 1970, ENGAN and AUBERT 1971). DREWS *et al.* (1969) showed that Triton X-305 was an effective stationary phase. In the separation parameters given below, a polar diglycerol column was coupled in series with the Triton X-305 column to

retard interfering polar components like ethanol.

Columns (in series) : (i) 25% diglycerol on 60–80 mesh Chromosorb W (AW. DMCS), 1 m  $\times$  3.12 mm, copper.  
(ii) 10% Triton X-305 on 80–100 mesh Chromosorb G (AW. DMCS), 6 m  $\times$  3.12 mm stainless steel.

Detector Temperature : 180 °C.

Column Temperature : 20 °C (isothermal).

Carrier gas : Nitrogen at 25 cm<sup>3</sup> min<sup>-1</sup>.

The gas chromatograph was equipped with an external 10 cm<sup>3</sup> stainless steel sampling loop fitted with a two-way valve to reroute the carrier gas through the loop and flush the sample into the separating columns.

## 2. Internal standardization

Dichloromethane was used as internal standard. A solution of 2.25 g dichloromethane/l in 50% (v/v) ethanol was used as working standard. A DMS stock solution of 50 mg/l in 50% (v/v) ethanol was prepared daily and used to make up the standards.

The relative response factors of DMS and dichloromethane were obtained with a saturated solution of potassium bitartrate of 12% (v/v) ethanol to which DMS was added such that the solutions contained 25–500  $\mu$ g/l. Dichloromethane was added to DMS standards so that its concentration was 3 mg/l in each.

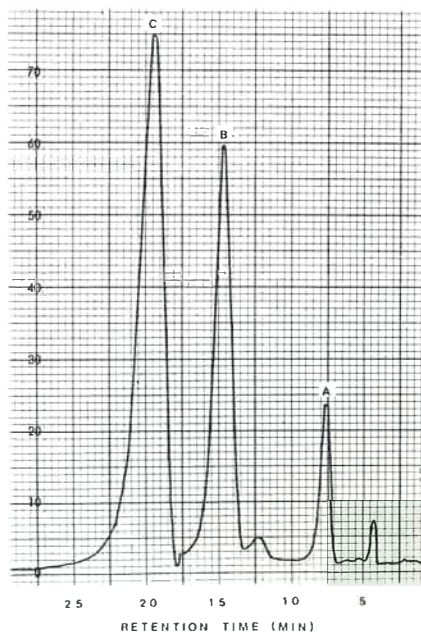
## 3. Headspace sampling

A bottle of wine (750 cm<sup>3</sup>), chilled to 0 °C, was opened and 1.0 cm<sup>3</sup> of dichloromethane solution added and mixed. The wine thus contained 3 mg/l of the internal standard.

To 20 g AR anhydrous ammonium sulphate in a dry 50 cm<sup>3</sup> conical flask was added 25.0 cm<sup>3</sup> of wine and immediately sealed with a rubber septum. The flask was then held in a water bath at 40 °C for 15 minutes. It was then removed and vigorously shaken in a mechanical shaker for 5 minutes and subsequently replaced in the water bath for a further 10 minutes. Immediately thereafter, 10 cm<sup>3</sup> of the headspace vapour

Chromatogram of typical separation of dimethyl sulphide in wines. Peak A is dimethyl sulphide (attenuator =  $2 \times 10^2$ ), peak B dichloromethane internal standard (att. =  $2 \times 10^2$ ) and peak C probably ethyl acetate (att. =  $1 \times 10^3$ ).

Chromatogramm einer typischen Dimethylsulfid-Trennung in Wein. A = Dimethylsulfid (Abschwächung  $2 \times 10^2$ ), B = Dichlormethan als Standard (Abschw.  $2 \times 10^2$ ), C = wahrscheinlich Äthylacetat (Abschw.  $1 \times 10^3$ ).



was withdrawn through the septum with a gas-tight hypodermic syringe and injected into the sampling loop. The carrier gas was then routed through the loop.

#### 4. Identification of DMS peak

The DMS peak was initially identified by its marked and strong odour, the use of retention times and mass spectrometry (DU PLESSIS *et al.* 1974). Subsequent identification was based on odour and retention time.

#### 5. Analysis of wines

The finalized method was subsequently applied to wines made from several cultivars and of different vintages.

### Results and Discussion

The addition of inorganic salts to increase vapour pressure of volatile compounds in dilute aqueous solutions is standard procedure in headspace analysis (NELSON and HOFF 1968, NAWAR 1971). The use of anhydrous sodium sulphate and sodium chloride have been reported (BASSETTE *et al.* 1962, SINCLAIR *et al.* 1969, 1970, ANONYMOUS 1971). The effectiveness of the latter two salts as well as anhydrous ammonium sulphate were examined in the same wines at various concentrations. Using

Table 1  
Efficiency of dimethyl sulphide analysis of wines  
Die Zuverlässigkeit der Dimethylsulfid-Bestimmung bei Weinen

Wine	Dimethyl sulphide				Standard deviation $\mu\text{g/l}$	Standard deviation %
	Added $\mu\text{g/l}$	Found				
		(i) $\mu\text{g/l}$	(ii) $\mu\text{g/l}$	%		
1 and 2	50	49	51	100,0		
	100	93	97	95,0		
	200	195	199	98,5		
	300	292	313	101,0		
Average <sup>1)</sup>	162,5	157,3	165,0	—	6,3	3,9
3 <sup>2)</sup>	—	15	14	93,3		
4	—	26	27	103,8		
5	—	11	13	118,2		
6	—	11	12	109,1		
7	—	40	38	95,0		
8	—	79	76	96,2		
9	—	485	464	95,7		
Average	—	95,3	92,0	—	5,7	6,0
Average <sup>3)</sup>		117,8	118,8	—	6,8	5,7

<sup>1)</sup> Data from 2 different wines; percentage determined from an average of columns (i) and (ii).

<sup>2)</sup> Duplicate analysis, percentage determined in terms of column (i) data.

<sup>3)</sup> Data from columns (i) and (ii).

DMS peak heights as basis, the highest recoveries were achieved with 20 g of ammonium sulphate per 25 cm<sup>3</sup> sample. These values were 20% and 35% higher, respectively, than that achieved with saturation with sodium sulphate and sodium chloride.

A typical chromatogram of a wine is given in the figure. The concentration of DMS was determined on peak area and response factors in relation to the internal standard. Recoveries and reproducibility in wines were satisfactory. Pertinent data from nine wines are given in Table 1.

The data of the analysis of several wines by the developed method is given in Table 2. In general, it appeared that DMS developed with maturation of wines since all but one of the 1974 wines did not contain DMS. As the wines matured, however, DMS concentration increased and the so-called bottle bouquet also increased. In fact, wines which in sensory evaluations were rated by judges to have

Table 2

Dimethyl sulphide concentrations in different cultivar wines of different years  
Dimethylsulfid-Konzentration in Weinen verschiedener Sorten aus verschiedenen Jahrgängen

Vintage year	Cultivar	Dimethyl Sulphide µg/l
1974	White French (Palomino)	0
	Vital	10
	Steen (Chenin blanc)	0
	Steen (Chenin blanc)	0
	Kerner	0
	Colombar	0
1973	Frontignan	6
	K2	15
	Steen (Chenin blanc)	12
	Steen (Chenin blanc)	0
	Steen (Chenin blanc)	37
	Green grape	0
	Colombar	40
Colombar	19	
1972	S. du Pulliat	11
	Steen (Chenin blanc)	27
	Steen (Chenin blanc)	12
	Steen (Chenin blanc)	47
	Colombar	46
	Riesling	97
	Riesling	147
	Riesling	85
	Riesling	474
"Late Harvest"	77	
"Late Harvest"	38	

bottle bouquet, all showed appreciable concentrations of DMS. A further interesting point was that Riesling and "Late Harvest" wines were especially inclined to develop DMS.

The method developed for DMS determination in wines gives wholly satisfactory results. Since small quantities of DMS in wines can contribute effectively to bouquet, this method can be applied as one facet in the quality determination of wines.

### Summary

A gaschromatographic headspace method has been developed for the quantitative determination of dimethyl sulphide (DMS) in wines. The standard deviation of the method was in the order of 6%.

Application of the method to the analysis of several white wines showed DMS values which varied from 0 to over 400  $\mu\text{g/l}$ . From analytical data it appeared that DMS developed in the bottle and could as such possibly contribute to bottle bouquet. It was found that matured Riesling wines had particularly high concentrations of DMS.

### Literature

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