

# Gas Chromatography

**Subcommittee Members:** R. Williams, *Chairman*; R. Bogenrief, P. Friese, M. Moll (*EBC*), M. Morrison, N. Mundy, S. Rader, M. Waxman, and D. W. Hysert (*ex officio*).

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## CONCLUSIONS

1. The flame ionization detection method (FID) (7) for dimethyl sulfide (DMS) in beer contained several serious shortcomings in its description, which made it unworkable for many collaborators. The limited data received by reporting collaborators indicated a reasonable within-laboratory agreement for the sample pairs.
2. The flame photometric detection method (FPD) (4) for dimethyl sulfide (DMS) in beer indicated a large coefficient of variation of between-laboratory error relative to that of within-laboratory error, suggesting that, although the method is sound, the detail provided in the published methodology contains basic shortcomings.

## RECOMMENDATIONS

1. Because the flame ionization detector has been used routinely in U.K. and North American brewing laboratories for the analysis of DMS in beer (1,5,6,7), the method evaluated (7) should be reassessed by the authors to provide the necessary added detail in method description to make it more amenable to collaborative testing. (See Supplement to this report.)
2. The flame photometric detection method for DMS in beer (4) should be reassessed by the authors to append the necessary extra detail in method description to minimize between-laboratory error. Further collaborative testing should follow. (*J. Am. Soc. Brew. Chem.* 40(3):118, 1982).
3. Ruggedness testing on both FID and FPD method should be done.

At the May, 1981 Annual Meeting in Miami, the Technical Committee recommended that this subcommittee collaboratively evaluate two published methods (4,7) for the determination of dimethyl sulfide (DMS) in beer.

## PROCEDURES

Four 40-L quantities of lager beer containing an endogenous level of 60  $\mu\text{g/L}$  DMS as measured by the proposed FID and FPD methods were collected from a bright beer tank. Two of these were individually adjusted to approximately 75  $\mu\text{g/L}$  DMS and the remaining two similarly adjusted to approximately 100  $\mu\text{g/L}$  DMS. These sample pairs were bottled, pasteurized, and sent to the collaborators as pairs A-B and C-D, respectively. The results of analyses by collaborators on these beer sample pairs would thus be amenable to the Youden Block statistical design (5). Collaborators were required to prepare their own column packings, pack and condition their own columns, acquire their own reagents, and make the necessary calibrations for either or both methods, using products from their respective breweries, before analyzing the test samples.

## RESULTS AND DISCUSSION

### Flame Ionization Detection Method

Only three sets of results (Table I) were submitted for this method, too few to assess statistically. One other collaborator, who

devoted much time to this method, was unable to resolve the DMS and internal standard peaks away from other interfering components. Another collaborator reported the inability to identify DMS either in "spiked" beers or in aqueous solution. The limited data submitted and the observations show that the flame ionization detection method is seriously lacking in detail in the published methodology. As it stands, the method is unsuitable for collaborative testing.

### Flame Photometric Detection Method

Seven sets of results were obtained for this method, which are also tabulated in Table I. Obviously, a wide range exists in the values reported for either pair of beers, which leads to a high between-laboratory error in both, as indicated in Table II, the statistical summary for this method. The within-laboratory errors for both pairs are reasonable, however, which suggests that the method is viable but lacking detail in its description, leading to these high between-laboratory errors.

One specific instruction inadvertently omitted from the published method was that the authors would stipulate that the gas chromatography column be thoroughly conditioned with DMS before being used for DMS analysis. This is a potential source of between-laboratory error. Another might be the lack of detail in the description for preparation of DMS addition solutions. Should these be made up w/v or v/v? Also, because of the volatility of DMS (b.p. 37–38°C), should the diluting solvent be chilled and, if so, to what temperature?

If these and other potential-problems were to be standardized in all laboratories, a significant improvement in between-laboratory error could result.

## SUPPLEMENT

The authors of the paper on application of the FID procedure to DMS evaluation (7) have provided the following supplemental details for column conditioning and stock DMS solution preparation.

Nonsilicized glass wool was used at both ends of the column. The column was preconditioned at 200°C with the detector end

TABLE I  
Dimethyl Sulfide in Beer: Individual Data<sup>a</sup>

Collaborator	Method 1 <sup>b</sup>				Method 2 <sup>c</sup>			
	Pair 1 A	Pair 1 B	Pair 2 C	Pair 2 D	Pair 1 A	Pair 1 B	Pair 2 C	Pair 2 D
1					55	56	75	75
2					83	85	114	113
3	72	76	108	105	72	73	106	106
4					67	66	93	92
5					71	77	124	119
6	33	32	56	55	15	14 <sup>d</sup>	40	30
7	39	43	57	74	42	66	68	68
Mean <sup>e</sup>	48	50	74	78	65	70.5	88.6	86.1
Grand mean		49		76		67.8		87.4
Theoretical DMS		75		110		75		110
Percent DMS recovered		65.3		69.1		90.4		79.5

<sup>a</sup>  $\mu\text{g/L}$ .

<sup>b</sup> Flame ionization detection method.

<sup>c</sup> Flame photometric detection method.

<sup>d</sup> Rejected as outlier. Dixon's test,  $P \leq 0.05$ .

<sup>e</sup> Means do not include outliers.

**TABLE II**  
**Dimethyl Sulfide<sup>a</sup> in Beer by Flame Photometric Gas Chromatography:**  
**Statistical Summary**

Pairs	No. of Laboratories	Grand Mean <sup>b</sup>	Error			c.v. (%) <sup>e</sup>	Calc. F <sup>c</sup>	Critical F <sup>f</sup>
			Within-Laboratory <sup>c</sup>	Between-Laboratory <sup>c</sup>	Combined <sup>d</sup>			
A-B	6	67.8	6.6	10.6	12.5	18.4	6.09	5.05
C-D	7	87.4	2.7	30.2	30.3	34.7	256.0	4.28

<sup>a</sup>  $\mu\text{g/L}$ .

<sup>b</sup> Grand mean =  $\text{GM} = (\bar{A} + \bar{B})/2$  or  $(\bar{C} + \bar{D})/2$ .

<sup>c</sup> Calculated per Youden and Steiner (8).

<sup>d</sup> Combined error ( $S_c$ ) calculated from within-laboratory error ( $S_r$ ) and between-laboratory error ( $S_b$ );  $S_c = \sqrt{S_r^2 + S_b^2}$ .

<sup>e</sup> Coefficient of variation of  $S_c = 100 (S_c/\text{GM})$ .

<sup>f</sup> Critical F from tables of F distribution (3) at  $P \leq 0.05$ .

disconnected for a minimum of 24 hr and with a carrier flow of  $>60$  ml/min. The detector end of the column was connected and chemically conditioned to DMS by making repeated injections of DMS vapor (headspace from reagent bottle) run isothermally at  $70^\circ\text{C}$ . Repeated injections of beer headspace samples prepared and analyzed as outlined were then made to sample-condition the column prior to calibration runs. During these preliminary runs, the column flow was adjusted so that DMS eluted at about 3.2 min and the internal standard at about 7.4 min.

For preparation of DMS stock solution, the appropriate volume of DMS ( $0-4^\circ\text{C}$ ) was added to 50 ml of cold ( $0-4^\circ\text{C}$ ) 5% aqueous ethanol in a 100-ml volumetric flask using a microliter syringe. The syringe needle was held below the surface of the ethanol solution and the DMS added slowly to prevent loss. The flask was made to slightly under volume with cold ( $0-4^\circ\text{C}$ ) 5% ethanol and after attemperation at  $0-4^\circ\text{C}$  was adjusted to exact volume again with cold 5% ethanol.

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