

CHROM. 4038

Flame photometric determination at the parts per thousand million level of some volatile sulphur compounds

Volatile sulphur compounds have, in many cases, exceedingly low taste thresholds^{1,2} and their production during fermentation can markedly affect the taste of beer even at the parts per hundred million level. Their determination is, therefore, of considerable importance. Until very recently, the only published methods for the determination of volatile sulphur compounds in beer have involved either (a) distillation, or (b) sweeping beer with a stream of inert gas, trapping the volatiles and measuring them absorptiometrically. Results obtained by these methods give conflicting pictures. Possible sources of error arise in (a) conversion of non-volatile precursors to sulphur volatiles during distillation or isolation, (b) non specificity of the absorptiometric procedures and (c) oxidation and exchange reactions. HASHIMOTO AND KUROIWA³ detected thioformaldehyde, dithioformaldehyde and thioacetone in beer by sweeping the volatiles from cooled beer with nitrogen and trapping in an acid mercuric chloride solution. They analysed the mercuric mercaptides by gas-liquid chromatography after flash exchange with toluene-3,4-dithiol. Thiols were not detected in any beers they examined.

Identification of sulphur volatiles which are based solely on gas chromatographic retention times may be regarded with some suspicion. The development of the highly specific and sensitive flame photometric detector⁴ appeared to offer hope of more specific determination of the sulphur volatiles of beer. The results reported here show this hope to be justified, and the method should be applicable to any aqueous solution.

In the first instance, we have applied the flame photometric detector to the determination of sulphur volatiles in beer headspace vapour samples. Use of headspace vapour samples avoids complications arising from preliminary concentration or isolation procedures.

Experimental

Detector. The Melpar Flame Photometric Detector was used⁴. This measures the optical emission of sulphur compounds in a hydrogen rich flame, using a 526 m μ interference filter and a photomultiplier. It was operated at 150°.

Oven. The oven portion of a Griffin and George flame ionization gas chromatograph with the flame photometric detector mounted on top. Oven temperature 50°.

Amplifier. A Micro Tek dual channel electrometer was used to monitor simultaneously both the flame ionization and the flame photometric responses.

Gas supply. Nitrogen (carrier), hydrogen and oxygen were used at flow rates of 8, 150 and 20 ml/min respectively. An auxiliary nitrogen supply of 70 ml/min was applied at the instrument supplier's recommendation through a T piece on the carrier line to the detector.

Columns. A stainless steel capillary column 300 ft. long and 0.02 in. I.D. coated with polyethylene glycol 400 (Merck) was used.

Samples of 50 ml of beer and 1 ml of a 3 μ g/ml alcoholic solution of di-isopropyl sulphide (as an internal reference standard) were added to a 250 ml conical flask

containing 30 g of ammonium sulphate. The addition of ammonium sulphate causes an increase in the proportion of volatiles in the vapour phase. The flask was sealed with a "Subaseal" rubber closure and equilibrated in a water bath at 35° for 1 h. A 0.5 ml vapour sample was withdrawn with a hypodermic syringe and immediately injected into the gas chromatograph. Fig. 1 shows a typical chromatogram obtained.

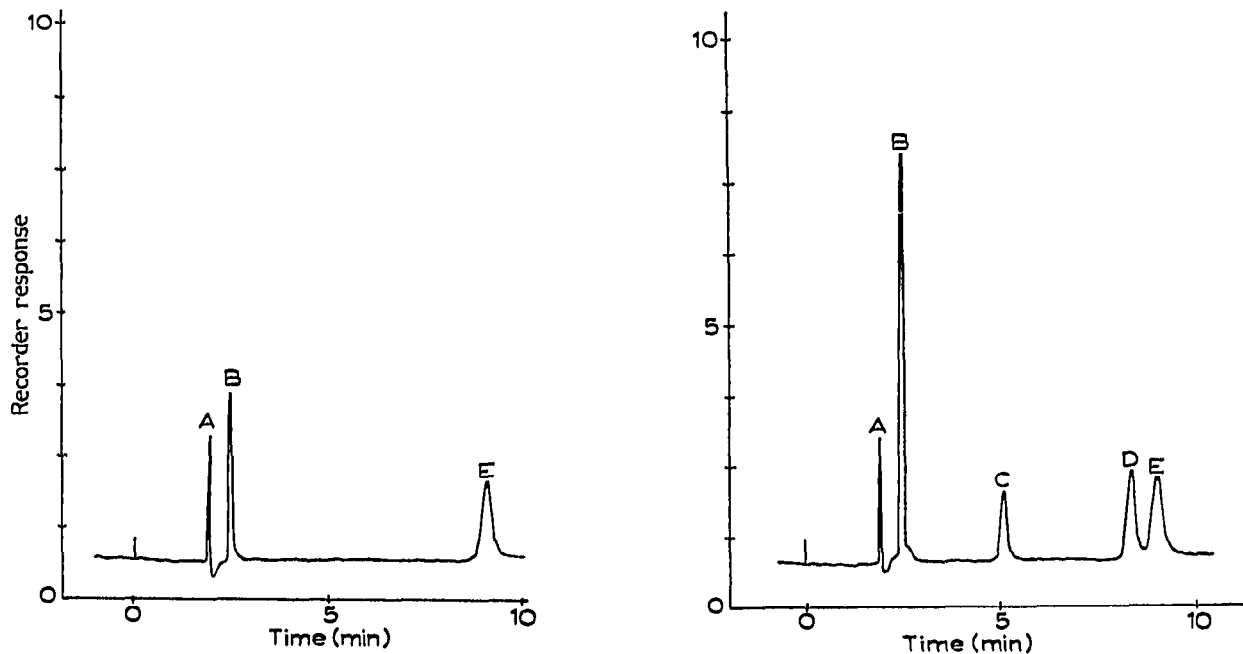


Fig. 1. A 0.5 ml vapour sample of beer with standard addition of 0.06 p.p.m. di-isopropyl sulphide (peak E). For peak A see text. Peak B, dimethyl sulphide.

Fig. 2. A 0.5 ml vapour sample of beer with 0.03 p.p.m. added dimethyl sulphide (peak B); 0.03 p.p.m. added diethyl sulphide (peak C); 0.02 p.p.m. added dimethyl disulphide (peak D); 0.06 p.p.m. added di-isopropyl sulphide (peak E). For peak A see text.

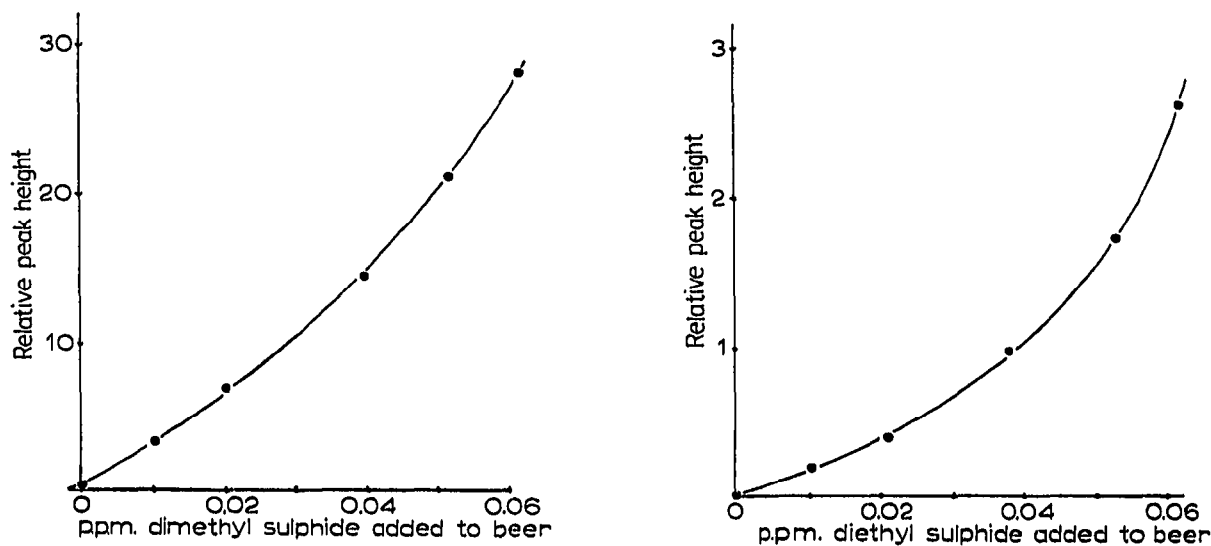


Fig. 3. Calibration curve for dimethyl sulphide added to beer. The negative intercept on the x-axis is due to the endogenous dimethyl sulphide content of the beer.

Fig. 4. Calibration curve for diethyl sulphide added to beer.

Quantitation was achieved by adding known amounts of freshly prepared alcoholic solutions of dimethyl sulphide, diethyl sulphide and dimethyl disulphide to beers which were then analysed by the procedure outlined. Fig. 2 shows a chromatogram obtained for a beer with additions of 0.03 p.p.m. dimethyl sulphide, 0.03 p.p.m. diethyl sulphide and 0.02 p.p.m. dimethyl disulphide. Figs. 3 and 4 show the non-linear calibration curves obtained for dimethyl and diethyl sulphides in beer. Sulphur compounds usually give non-linear calibration curves with this type of detector⁴.

Results

The only volatile found in significant amount in the headspace above beer was dimethyl sulphide. This was found in all samples of normal beer examined, the amount varying from 0.002 to 0.006 p.p.m. The identity of peak A in the chromatograms shown in Figs. 1 and 2 is not known but this would appear to be a sulphur volatile; no peak occurs in the corresponding flame ionization chromatograms. The peak is not due to hydrogen sulphide and occurs in all the flame photometric chromatograms obtained from beer. The diethyl sulphide content of all beers examined was less than the sensitivity limit, 0.005 p.p.m. The dimethyl disulphide concentration was also less than the sensitivity limit, 0.01 p.p.m.

Thiols and hydrogen sulphide were not reproducibly detected in headspace samples when added to beer or to water at the parts per 10^8 to 10^7 level using stainless steel columns. A 150 ft. nylon capillary column 0.015 in. I.D. coated with Span 80 when used for the determination of sulphides gave very similar results to the stainless steel column, but thiol recovery was virtually nil. Packed glass columns also gave no recoveries for thiols added to beer or to water at the parts per 10^8 to 10^7 level. This loss of thiols is thought to be due to interaction in the metal capillary tube used to connect the column exit to the detector. We are at present investigating whether measurement of low levels of thiols will become practicable if all metal is eliminated from the sample-plus-carrier gas pathway.

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