GAS CHROMATOGRAPHY

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Key words: *Beer volatiles, DMS, Free fatty acids, Residual solvents in can linings.*

CONCLUSION

1. No new methods for solvents associated with can linings have been published; consequently, no further work can be planned.
2. Considerable interest has been shown in the determination of dimethyl sulfide and several GC methods are available.

RECOMMENDATION

The subcommittee should evaluate gas chromatographic procedures for dimethyl sulfide (DMS) in beer. Methods using the flame ionization detector as well as the flame photometric detector should be tested.

RESULTS AND DISCUSSION

After having established in 1979–80 that a satisfactory method was available for chromatographing solvents associated with can linings (1), the subcommittee's assignment this year was to search for new methods for adapting the GC technique for the actual measurement of solvent residues in cans, or evaluate the need for GC methods in other areas (eg, DMS by headspace).

Members were polled regarding equipment and areas of interest for future collaborative work. Considerable interest was shown in the analysis of beer for fatty acids, for beer volatiles by extraction, and for DMS content. The poll further indicated that a sufficient number of electron capture and flame photometric detectors were available for collaborative trial employing either one of these detectors. Therefore, methods using either of these detectors during the 1981–82 work year could be evaluated.

Methods submitted by subcommittee members for consideration are as follows:

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Determination of Residual Solvents in Beer and Beverage Cans by Gas Chromatography

Two procedures were discussed by the subcommittee; however, neither one has been published so no action can be taken at this time.

Gas Chromatographic Determination of Beer Volatiles by Carbon Disulfide Extraction

Powell and Brown (7) originally reported on this method for the extraction of beer volatiles with carbon disulfide (CS_2). In the basic method, sodium chloride was added to carbonated beer which was then extracted with CS_2; 1-octanol was the internal standard. The two columns recommended for the separation were: 1) 12 ft × 1/8 in. o.d. stainless steel packed with 8% FFAP on Chromosorb G, AW, DMCS, and 2) 12 ft × 1/8 in. o.d. SS packed with 9% FFAP on Chromosorb W, AW, DMCS. Problems encountered with the original method include poor reproducibility, some tailing of the polar compounds, and short column life.

Stenroos, Siebert, and Meilgaard (8) found that decreasing the amount of sodium chloride added, use of a different column packing, and better control of conditions improved the reproducibility of this analysis. The column used was 6 ft × 2 mm i.d. glass packed with 20% Carbowax 20 M on Chromosorb P, 80/100 mesh; this column gave better resolution, less tailing, and longer column life.

A number of the collaborators reported that they are working with the general extraction procedure but using capillary columns for the separation. Generally, solvents other than CS_2, such as freon 113 and chloroform, are being used. CS_2 can cause rapid deterioration of certain columns and may cause some detector jets to become plugged.

Determination of Free Fatty Acids in Beer

This method by Chen, Jamieson, and Van Gheluwe (2) is a modification of the one described by MacPherson and Buckee (6). They were able to reduce the total number of solvent and alkaline extractions required from 6 to 2. A 6-ft stainless-steel column, 1/8 in. o.d., packed with 10% SP 2330 on Chromosorb W, AW was used to chromatograph fatty acids with carbon numbers from 8 to 22.

DMS in Beer and Malt

Several procedures have been published recently for the analyses of DMS in beer and malt. The majority of techniques use the flame photometric detector (FPD) which is both fast and sensitive. A method using the flame ionization detector (FID) has also been published; while not as rapid as methods using the FPD, it would be useful to laboratories not equipped with a FPD.

DMS in Beer using FPD

The method by Hysert, Morrison, and Jamieson (3) takes the headspace sample directly from the bottle or can with a clamping platform or can piercer (Altech Associates). Ethyl methyl sulfide (EMS) in 50% aqueous ethanol is the internal standard. An 18 in. × ¼ in. o.d. glass column packed with acetone-washed Porapak QS allows analysis to be completed in less than 5 min. The relative standard deviation from replicate analyses of bottled beer is 3%.

DMS in Malt using FPD

In this assay for both free DMS and dimethyl sulfide percursor (DMSP) in malt, Hysert, Weaver, and Morrison (4) used the same gas chromatographic headspace technique previously described (3). A malt extract is prepared and after centrifuging, the supernatant liquid is transferred to a 120-ml hypovial along with the EMS internal standard. The capped vial is shaken 15 min in a 20°C water bath and a headspace sample injected on the column.

The DMSP level in malt is established by difference. Total free DMS plus DMSP are determined after heating the supernatant malt extract with 10*N* NaOH in a boiling water bath for 1 hr. This material is transferred to a hypovial and the analyses continued as described above for free DMS. The formula for DMSP content is: DMSP = (DMS + DMSP) − (DMS)

DMS in Beer and Wort using FID

The FID was used by Szlavko and Anderson (9) to analyze for DMS in beer as well as DMS and DMSP in wort. DMS in beer is determined by taking headspace samples from serum bottles containing beer, methyl propionate (internal standard), anhydrous sodium sulfate for the salting-out effect, and hydroxylamine hydrochloride to remove acetaldehyde. The column is 7 ft glass × ¼ in., packed with 10% Carbowax 20 M on Chromosorb P; separation of the compounds of interest took 8 min, but it was necessary to await the elution of the higher boiling beer compounds before another sample could be injected. A precision of 1% relative standard deviation was achieved on replicate samples of the same beer.

The method for the analysis of free DMS and DMSP in wort is basically the same as that of Hysert, Weaver and Morrison (4). Differences between the two methods are minor; they consist of filtration rather than centrifugation to separate the supernatant extract from the malt and changes in sample size. Chromatography was done on the same column used for beer with the FID.

Determination of Low Concentrations of Volatile Sulfur Compounds using FPD

Leppanen, Denslow, and Ronkainen (5) used a Chromosorb 101 trap to concentrate the sulfur volatiles from 200 ml of beer in a thermostated 350-ml sampling bottle. After purging the sample for 15 min, the trap was disconnected and immediately coupled to the chromatographic column with a Swagelok Quick-connect. A 4 m × 2 mm i.d. column packed with 12% DC-200 on Chromosorb W, AWS was used to separate DMS, methyl ethyl sulfide (internal standard), and dimethyl disulfide in 8 min. The authors state detection limits for sulfur compounds in a 10% w/w ethanol/water mixture were 2 μg/L for DMS and 0.1 μg/L for dimethyl disulfide.

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