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Note

Determination of diethylene glycol in wine

Rapid purification with a Carbopack B cartridge and quantitation by gas chromatography

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Very recently, the detection of a hazardous additive in wine, diethylene glycol (DEG), prompted a search for a reliable, gas chromatographic (GC) procedure able to determine small amounts of DEG in wine.

The determination of glycols in aqueous solution by GC is difficult as almost all stationary phases are intolerant to water and solid supports are insufficiently inert to achieve elution of glycols as untailed peaks. Further, the determination of DEG in wine is made even more difficult by the presence of endogeneous, high-boiling compounds which, on accumulating in the initial part of the column packing, induce partial chemisorption of DEG, which can give rise to "ghosting" effects.

The aim of this work was to devise a reliable and sensitive GC procedure able to determine DEG in wine. Rapid sample purification was achieved passing 2 ml of a wine sample through a Carbopack B[1–4] cartridge. Subsequently, 2 μl of the last 500 μl of the eluate were injected into the GC column containing Carbopack C modified with 0.8% (w/w) of tetrahydroxyethylethylenediamine (THEED), which is able to elute glycols as untailed peaks[5].

EXPERIMENTAL

Purification apparatus

The Carbopack B trap is an experimental kit developed and kindly supplied by Supelco (Bellefonte, PA, U.S.A.). The cartridge consists of a cylindrical polypropylene tube which is one-sixth full of 250 mg of Carbopack B graphitized carbon black with a particle size less than 125 μm. Polyethylene frits are located above and below the Carbopack B bed to hold the minute particles in place and keep the chromatographic column intact. This cartridge fitted directly into the vacuum manifold. Vacuum was obtained with a water pump, taking no care to ensure low and constant flow-rates of the samples percolating through the cartridge.

Purification procedure

The Carbopack B cartridge was cleaned by passing 5 ml of water, then 1.5 ml of the sample, to which had been added 1 g/l of 1,4-butanediol as an internal stan-

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dard, was passed through the cartridge and the effluent was discarded. A further 0.5 ml of the wine sample was passed through and the effluent was collected, and 2 μl of this eluate were injected into the GC column.

GC instrumentation

GC analysis was performed on a DANI (Milan, Italy) Model 3400 gas chromatograph equipped with a flame ionization detector. The glass column (1.0 m × 2 mm I.D.) was packed with Carbopack C graphitized carbon black, modified with 0.8% of THEED (Supelco). The GC column was conditioned overnight under flow, by holding the injector, detector and oven temperatures at 120°C. The column was operated by maintaining the same temperature conditions as used for the column conditioning. The operating temperature was critical in order to ensure a long life of the column. When the injection temperature was set at 130°C, we observed a slow but continuous degradation of the column packing, resulting in changes in the retention time of DEG and the appearance of some glycol peak tailing. Helium was used as the carrier gas. The dead time was 5 s.

RESULTS AND DISCUSSION

The effect on the GC packing of repeated injections of unpurified wine was evaluated. Several runs, each consisting of 30 injections of 2 μl of a red wine sample spiked with 2 g/l of DEG, were made. After each run, 2 μl of the same wine sample, but not fortified with DEG, were injected into the GC column. In the latter instance the chromatogram showed one "ghost" peak having the same retention time as DEG and apparently corresponding to a DEG content in wine of about 0.15 g/l. Moreover, after four injection runs, some glycol peak tailing appeared. Probably progressive accumulation on the injection port of unknown, high-boiling compounds present in wine are responsible for these two effects.

The same experiment was repeated by injecting a wine sample that had been submitted to the purification step described under Experimental. After each injection run we observed a "ghost" peak corresponding to a constant DEG concentration not exceeding 0.013 g/l. Further, no ghost peak was observed after a second injection of wine that had not been fortified with DEG. The extent of DEG "ghosting" measured after wine purification is certainly very low and it may be considered negligible in comparison with the level of DEG usually detected in adulterated wines. Anyway, in order to eliminate completely the presence of a "ghost" peak for DEG, we found it useful, after GC analysis of a sample containing a high concentration of DEG and before chromatographing another wine sample, to inject 2 μl of water containing 1 g/l of ethylene glycol. In this way, even traces of DEG remaining chemisorbed on the initial part of the columns were completely displaced by ethylene glycol.

Another advantage of injecting purified wine samples over injecting unpurified samples is that the life of the column packing is substantially prolonged. Even after 180 injections of purified wine during 1 week of operation, the chromatographic characteristics of the column packing remained unaltered and the peak for DEG showed no tailing.

Glycerol, which is a natural product present in wine in relatively large amounts, co-eluted from the Carbopack B cartridge with DEG and 1,4-butanediol. Under our

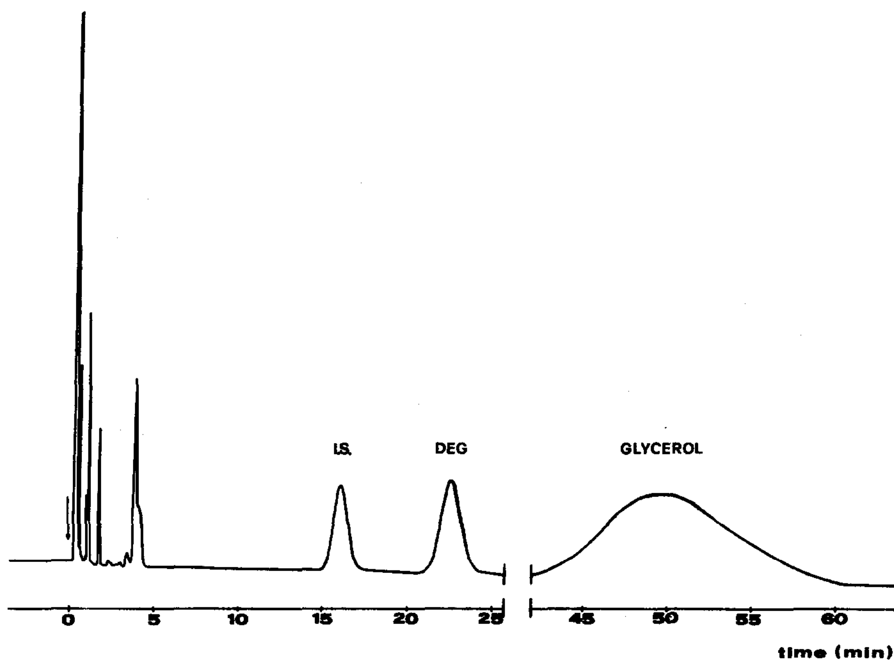

Fig. 1. Typical chromatogram of purified wine spiked with 2 g/l of DEG.

GC conditions, glycerol has a much higher retention time than DEG, and it is eluted as a very broad peak. This may cause interference during successive GC analyses. This problem was eliminated by injecting wine samples at constant intervals of 30 min. In this way, the peak for glycerol appeared in a zone of the chromatogram free from the two peaks for DEG and the internal standard.

Fig. 1 shows a typical GC profile for a purified wine sample spiked with DEG.

The recovery and precision of the method were assessed by analysing wine samples spiked with known amounts of DEG of 5, 2, 0.6 and 0.1 g/l. The recovery was calculated by measuring the peak heights of DEG relative to those of the internal standard and comparing them with those measured by direct injections of wine samples that had not been purified. Six replicate analyses at each DEG concentration gave an average recovery of 99.2% (range 96.9–102%). The coefficients of variation (C.V.) were 2.8 and 1.4% for the lowest and highest concentrations considered, respectively. The limit of sensitivity (signal-to-noise ratio = 3) at which DEG could be measured with a C.V. of 6.9% was 1 mg/l. At this concentration, a well defined chromatographic peak for DEG could still be obtained.

The specificity of the assay was evaluated by analysing 30 different DEG-free wine samples. No detectable peak having the retention time of DEG was observed. Moreover, adsorption studies were performed on the effectiveness of the Carbopack B surface to retain compounds dissolved in a wine-simulating aqueous solution, *viz.*, water–ethanol (88:12, v/v). The results showed that only very polar compounds, such as the lower members of mono- and polycarboxylic acids, alcohols, ketones, aldehydes and hydroxy and keto acids, passed almost unretained through the Carbopack

B cartridge and were co-eluted with DEG. However, these compounds are not potential sources of interference in the analysis as, when injected on to the above GC column packing, some of them were eluted with retention times much lower than that of DEG and the others were not detectable under the GC conditions chosen.

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