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Note

Simplified routine method for the determination of diethylene glycol in wines by capillary gas chromatography with flame ionization detection

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Diethylene glycol (DEG) has received much news media attention recently because of its finding in certain wines at levels often exceeding 100 mg/l. It is not permitted as a food additive in Canada and other countries, thus its presence in wines as a result of deliberate addition is illegal. Although DEG is not an extremely toxic substance it has been linked to liver and kidney damage if consumed in large quantities[1,2]. The Canadian Department of Health and Welfare has recently set an interim "actionable level" of 10 mg/l based on a review of the toxicology data.

The most useful methodology to date for DEG has been capillary gas chromatography (GC)[3–6]. Direct injection of wine[4,7] in our experience has led to rapid deterioration of the chromatographic separation and a need to clean the inlet system after only a few sample injections. Sequentially coupled columns have been evaluated for improved analysis by capillary GC but require a rather specialized chromatographic system[7]. Trimethylsilyl[8,9] and heptafluorobutyryl[10] derivatives of DEG have also been examined by GC and GC–mass spectrometry (MS). However, these reactions require extraction from aqueous solution or evaporation before derivatization. Extraction of DEG from aqueous solutions is difficult resulting in low recoveries[3]. Several cleanup techniques have been described using combinations such as barium hydroxide–acetone[11], diethyl ether–sodium carbonate–acetone[12], ion exchange[8], Extrelute columns[13], or an experimental cartridge packed with Carbopak B (ref. 14).

The present work describes a simple cleanup technique that requires no extraction or derivatization for the capillary GC determination of DEG in wines, employing flame ionization detection (FID). The approach has already proved to be successful when GC–MS was used for the determination[15].

EXPERIMENTAL

Reagents

Standards of DEG (Fisher, reagent grade) were prepared in 10% aqueous ethanol to yield DEG concentrations in the range of 0.5–50 μg/ml. The analytical working standards were prepared by adding known quantities of DEG to a blank wine sample and treating the mixture as described under *Sample preparation*. (The

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blank wine was found to contain 0.23 mg/l of DEG by GC–MS. This level was well below the detection limit obtained by GC–FID.) All solvents were distilled-in-glass or reagent-grade materials.

Sample preparation

A 1-ml volume of wine was placed in a 5-ml centrifuge tube followed by the addition of *ca.* 30 mg of decolourizing charcoal (Darco-G-60, J. T. Baker). The mixture was shaken on a vortex mixer for a few seconds and the charcoal allowed to settle. A 200-μl aliquot of the decolourized wine was transferred to a 3-ml vial and diluted with 800 μl of acetonitrile. The solution was mixed, cooled in an ice-water bath for about 15 min and filtered through a 0.45-μm filter (Millipore Millex-GV syringe filter unit). A 1-μl volume of the filtrate was injected into the GC system.

Gas chromatography

A Varian Model 3400 gas chromatograph equipped with a flame ionization detector and an on-column capillary injector was employed for the study. Separations were achieved on a DBWAX column (30 m × 0.32 mm I.D.; 0.15 μm layer thickness) (J and W Scientific) with the following temperature program: 70°C hold for 2 min, 50°C/min to 120°C, 5°C/min to 150°C, hold 2 min, 50°C/min to 230°C, hold 10 min. Injector program was: 80°C initial, 180°C/min to 230°C. Detector temperature was 240°C. Volumes of 1 μl of samples or standards were injected. Quantitation was based on peak heights.

RESULTS AND DISCUSSION

During method development it was found that DEG eluted as a much sharper and more reproducible peak when spiked in actual wine extracts. Thus for routine analysis a blank wine sample was spiked with various levels of DEG and used for quantitation. It was found in earlier work[15] employing a splitless injector (rather than on-column) that several injections of wine extracts were necessary before reproducible DEG peaks were obtained with standards. Similar problems with ad-

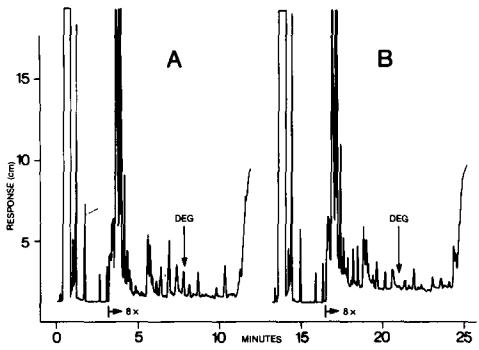

Fig. 1. Chromatogram of: (A) a red wine sample spiked with 10 mg/l DEG and (B) the same sample without DEG added. GC conditions as described in the text. Attenuation was 256× for 3 min then switched to 8×. Retention time of DEG, 7.8 min.

sorption of DEG on glass surfaces has also been reported[7,14]. In the present work we found that spiked wine extracts functioned very well as standards for quantitation. The final 10 min of the temperature program was used only to remove late eluting peaks before the next injection.

Fig. 1 shows results obtained with a blank and a spiked red wine using the charcoal–acetonitrile cleanup. The charcoal served to remove pigments and related compounds while the acetonitrile treatment caused precipitation of additional material, likely sugars. The resulting solution was very clean compared to the original wine. Although the experimental Carbopak B cartridges[14] were not available to us, we found the present procedure to be simple and cost effective. As can be seen from Fig. 1, DEG can be easily detected at the 10 mg/l level. DEG could be detected down to about 2 mg/l with FID employed. Although this is more than 10-fold less sensitive than GC-MS[15], it is nevertheless more than adequate for detecting 10 mg/l, the limit set by the Canadian government.

In order to evaluate the method, a number of red and white wines were purchased and analysed after carrying out the charcoal–acetonitrile cleanup. The same extracts were also analysed by GC–MS (as described earlier[15]) for comparison purposes. Table I lists the results. It can be seen that the FID results (above the detection limit) compare well to those obtained by GC–MS. The agreement indicates that the cleanup technique works well even for a non-selective detection system such as FID and that this detection system can be used routinely for DEG analysis in wines at levels as low as 2 mg/l. Fig. 2 shows typical chromatograms for three wine samples containing various levels of DEG. In earlier work[15] three internal standards were evaluated to aid quantitation. An internal standard was not used in the present work, although it is useful for monitoring reproducibility of injections, particularly when only 1–2 μl of sample are injected.

TABLE I

ANALYSIS OF WINE FOR DIETHYLENE GLYCOL

ND = Not detected, less than 1 mg/l.

Sample	*Results (mg/l)*	
	GC–FID	*GC–MS*
Red wines		
1	ND	0.23
2	ND	0.19
3	ND	0.22
4	ND	0.14
White wines		
1	4.4	3.8
2	29	31
3	1.6	1.0
4	ND	0.14
5	ND	0.20
6	6.1	6.4
7	ND	0.13
8	ND	0.10

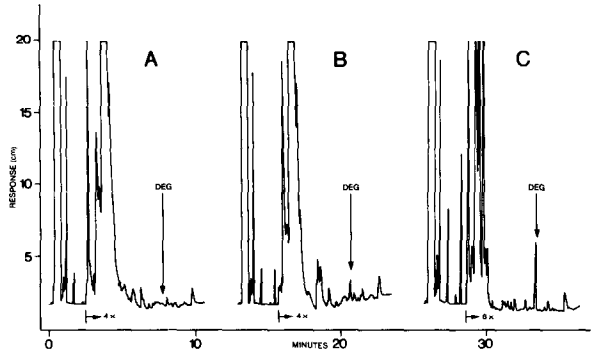

Fig. 2. Chromatograms of (A) a red wine sample containing less than 1 mg/l DEG, (B) a white wine sample containing 6.1 mg/l DEG, and (C) a white wine sample containing 29.0 mg/l DEG. Conditions as in Fig. 1 except in (A) and (B) where attenuation was switched to 4× after 3 min.

A very important additional advantage of the cleanup is that the extracts are clean enough to permit repeated analyses of wine samples with minimum deterioration of the chromatographic or detector system. In the present work about 50 injections of wine extracts were made with no loss of system performance. Using the same cleanup for GC–MS analysis over 200 wine samples have been analysed with no chromatographic or mass spectrometric instrument contamination[15].

In conclusion, the simple cleanup technique described in this work enables the routine determination of DEG in wine samples at levels as low as 2 mg/l. The results are in very good agreement with those obtained by GC/MS indicating its good potential for determining DEG in wines on a routine basis.

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