087

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Gas Chromatographic-Flame Ionization Investigation of 1,2-Propanediol (Propylene glycol) in Packaged and In-process Beer Samples

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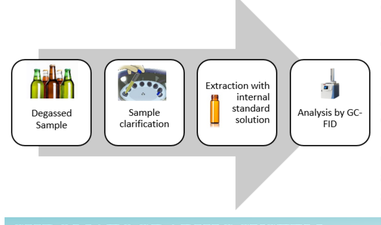
INTRODUCTION

An accurate analytical method for the identification and quantitation of propylene glycol in packaged and in-process beer is described.
From a food safety and quality perspective, propylene glycol, generally considered safe is bad for beer quality. Propylene glycol used in breweries is not typically food grade quality and may circulate in iron pipes for many years. Contamination from propylene glycol can lead to metal pick up (Fe, Mn, Cu) in beer which in turn can contribute to poor flavour stability and a lower shelf life (faster oxidation). From a regulatory point of view propylene glycol is not permitted as an additive unless used as part of a flavour system. The undeclared presence of propylene glycol above naturally occurring levels can lead to recalls of product if released out into the market.
Propylene glycol concentration in beer was determined using a simple methanol solvent extraction, using ethylene glycol as an added internal standard, with detection by capillary gas chromatography.
Chromatographic separation of propylene glycol was successfully achieved using a Restek 30 meter, 0.53 mmID, 1 µm df Stabilwax (Crossbond Carbowax polyethylene glycol) column with flame ionization using a Thermo Fisher Trace 1300 instrument.

BACKGROUND

Propylene glycol is a naturally occurring by product of fermentation and is also commonly used as a refrigerant in breweries. Traditional gas chromatographic methods of analysing propylene glycol show very poor chromatographic separation and high detection limits. This poster describes a chromatographic method for the simple, rapid, quantitative determination of propylene glycol with a lower detection limit of 5 mg/L.

SAMPLE PREPARATION



Samples were degassed by forceful swirling. When necessary, cloudy or turbid samples were clarified using centrifugation at 3500 rpm for 10 minutes (G force = 1465). A 1.0mL aliquot of the degassed/clarified sample was transferred to a 15mL amber glass screw top vial. After the addition of 3 mL of internal standard solution, each sample was capped and vortexed for 30 seconds. A portion of this mixture was then transferred to a 2mL gas chromatograph (GC) autosampler vial sealed with a screw top and analyzed using the chromatographic system described below.

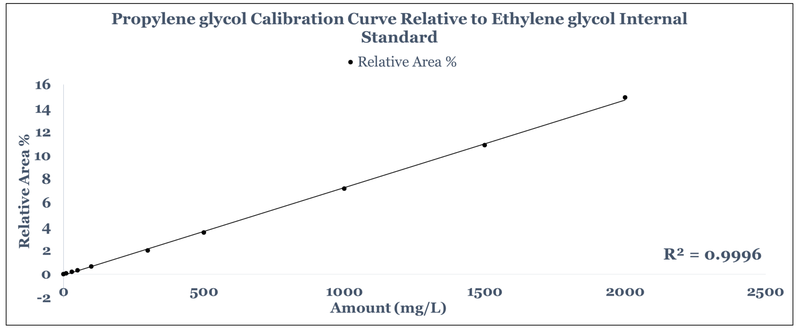
CHROMATOGRAPHIC SYSTEM

Thermo Fisher Trace 1300 GC

The chromatographic system consisted of a Thermo Scientific Trace 1300 GC with a Thermo Scientific™ Dionex™ Chromeleon™ CDS software system. The GC was equipped with capillary injector and detector fittings and a flame ionization detector (FID). A Restek Stabilwax (30 m X 0.53mm ID X 1µm film thickness) column was used to achieve separation. The initial oven temperature was 40°C (5-min hold) and was ramped at 40°C/min to a temperature of 140°C (0.5-min hold), then ramped again at 30°C/min for a final oven temperature of 250°C (5-min hold), yielding a total sample run of 13 minutes. The injector temperature was 250°C. Ultra-high purity grade Helium was used as the carrier gas. A splitless injection was used with an injection volume of 1µL. All injections were made with an autosampler. The FID temperature was 250°C. The detector was auto zeroed before each new injection.

CALIBRATION

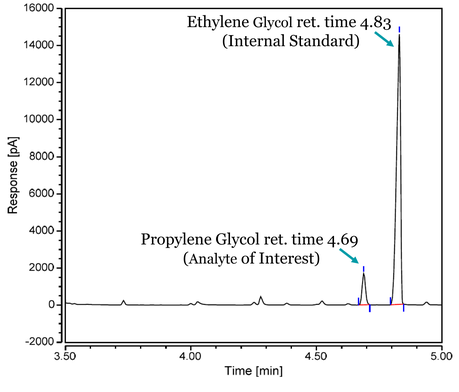
Additions of 0, 10, 30, 50, 100, 300, 500, 1000, 1500 and 2000 mg/L were selected to cover the ranges typically seen in beer and flavoured samples. A calibration curve was constructed for each compound by fitting the plotted data points to a least-squares regression line. The inverse of the slope of the line was taken as the response factor for that compound.



CALCULATION

The concentration of propylene glycol in an unknown sample was determined by multiplying the relative peak area obtained for propylene glycol by the response factor (RF).

$$Concentration\ (mg/L) = \frac{compound\ peak\ area}{internal\ standard\ peak\ area}(RF)$$



RESULTS AND DISCUSSION

TABLE I

Precision of 120 Replicates of Propylene Glycol in a Certified External Standard (4% Alcohol by Volume)

Compound	Minimum (mg/L)	Maximum (mg/L)	Mean (mg/L)	SD	cv (%)
Propylene glycol	45.00	54.20	49.14	2.03	4.12

120 replicates of a certified external standard were analyzed. Standard deviation for propylene glycol was 2.03. Coefficients of variation for propylene glycol were 4.12%

TABLES II and III

Recovery of 50 and 250 mg/L Propylene Glycol in 20 Replicates of Standard Lager Beer

Compound	Standard Addition	Recovery
Propylene glycol	50 mg/L	99.8%

Compound	Standard Addition	Recovery
Propylene glycol	250 mg/L	97.9%

Recovery was used as a measure of accuracy. Recovery was determined by analyzing a series of standard additions to standard lager beer.

Standard Lager (5% ABV, 4.00°SRM, 10BU, pH 4.13)

TABLE IV

Method Detection Limit and Limit of Quantification for Propylene Glycol

Compound	SD	MDL (3*SD)	Quantification Limit (10*SD
Propylene glycol	0.51	1.5 mg/L	5 mg/L

Method detection limits and quantification limits were determined by analyzing 10 replicates of a 1 mg/L propylene glycol standard. The method detection limit was calculated by multiplying 3 times the standard deviation. The quantification limit was calculated by multiplying 10 times the standard deviation.

SUMMARY

A method featuring simple, rapid solvent extraction and capillary gas chromatography permitted the quantitative determination of 1,2-Propanediol in packaged beer, in process beer (fermenting and aging) and cider. Recoveries for this analysis ranged from 97.9% to 99.8% and quantification limits for this analysis are down to 5 mg/L.