Gas Chromatographic Determination of 1,4-Dioxane at Low Parts-Per-Million Levels in Glycols

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Abstract

1,4-Dioxane is a flammable liquid and tends to form explosive peroxides. Its formation in glycols (low parts-per-million levels), which are used as dehumidifying agents in refineries, may take place by condensation. 1,4-Dioxane thus formed gets distilled over with benzene in the refinery process. Therefore, it is necessary to identify and determine the levels of 1,4-dioxane in glycols as well as benzene. Gas chromatography (GC) is probably the best technique for this purpose. GC analysis may be carried out using a flame ionization detector. Results show that 1,4-dioxane can be comfortably determined down to 2 ppm in glycols and benzene.

Introduction

1,4-Dioxane is a flammable liquid having a faint pleasant odor. Its vapors are harmful, and it tends to form explosive peroxides (1). The formation of 1,4-dioxane at low parts-per-million levels in glycols may take place during its manufacture. Under suitable dehydrating conditions, 1,4-dioxane is formed from two moles of ethylene glycol (2). Glycols are used in refineries in various extractive distillation processes for isolating and separating aromatics from naphtha streams, which produce a mixture of aromatics that are subsequently separated by distillation or fractional crystallization (3). The 1,4-dioxane present in glycols thus gets distilled over with benzene in the refinery processes. Therefore, it is necessary to determine 1,4-dioxane in glycols and benzene.

Experimental

Chemicals

High-performance liquid chromatographic (HPLC)-grade 1,4-dioxane, HPLC-grade benzene, HPLC-grade methanol, and analytical-grade ethylene glycol were obtained from Qualigens (A division of Glaxo, Mumbai, India), and HPLC-grade water was obtained from E. Merck (Mumbai, India).

Gas chromatographic analysis

Gas chromatographic (GC) studies were carried out using a CHEMITO 8610 GC (Toshniwal Instruments (India) Limited, Nashik, India) having one packed and one capillary injection port with a flame ionization detector (FID). A CHEMITO C-5000 data processor was used for data handling.

The packed columns used in this study were a 5% Carbowax 20M on an 80/100 mesh Chromosorb W (HP) stainless steel column (1.8-m × 3-mm o.d.) and a 10% OV-351 on an 80/100 mesh Chromosorb W (HP) stainless steel column (3-m × 3-mm o.d.). Both packed columns were prepared in the laboratory. The capillary column used in this study was a BP 20 (25-m × 0.32-mm i.d., 1.0-µm film thickness) from SGE (Ringwood Victoria, Australia).

Analytical conditions

For the 5% Carbowax 20M column, the carrier gas was nitrogen at a flow rate of 30 mL/min, the injection-port temperature was 200°C, and the detector-port temperature (FID) was 250°C. The oven temperature program began at 80°C, was held for 5 min, and then was raised to 210°C at 10°C/min. The range was ten times, and the attenuation was 1. The injection volume was 1 µL.

For the 10% OV-351 column, the carrier gas was nitrogen at a flow rate of 30 mL/min, the injection-port temperature was 200°C, and the detector-port temperature (FID) was 250°C. The oven temperature program began at 100°C, was held for 5 min, and then was raised to 240°C at 10°C/min. The range was ten times, and the attenuation was 1. The injection volume was 1 µL.

For the BP 20 capillary column, the carrier gas and the make-up gas was nitrogen with a gauge pressure of 1.4 bar, the injection-port temperature was 200°C, and the detector-port

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temperature (FID) was 230°C. The oven temperature program began at 70°C, was held for 6 min, and then was raised to 230°C at 10°C/min. The range was 1, and the attenuation was 8. The split rate was 15 mL/min, and the injection volume was 0.5 µL.

Solution preparation

Solutions of 2.5, 5.0, 10, 20, 30, and 100 ppm of 1,4-dioxane in water, methanol, and benzene were separately prepared fresh.

Solutions of 5 and 10 ppm of 1,4-dioxane were prepared in 50% ethylene glycol and 50% water, 50% ethylene glycol and 50% methanol, and benzene separately.

1,4-Dioxane solutions of 5 to 30 ppm in water were analyzed on Carbowax 20M and OV-351 columns under the conditions described previously. The typical chromatograms are shown in Figures 1 and 2. The retention time (RT) of 1,4-dioxane on the Carbowax 20M was approximately 1.3 min and on the OV-351 approximately 3.4 min. The linearity on both of the columns was good. The capillary column was used for analyzing 1,4-dioxane in methanol and benzene. The RT of 1,4-dioxane on a capillary column was approximately 5 min. The methanol solution showed a distinctly separated peak, and for benzene, the 1,4-dioxane peak appeared on the tail. The typical chromatograms are shown in Figures 3 and 4.

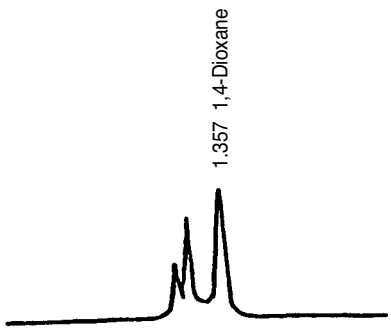

Figure 1. 1,4-Dioxane (2.5 ppm) in water on a Carbowax 20M column.

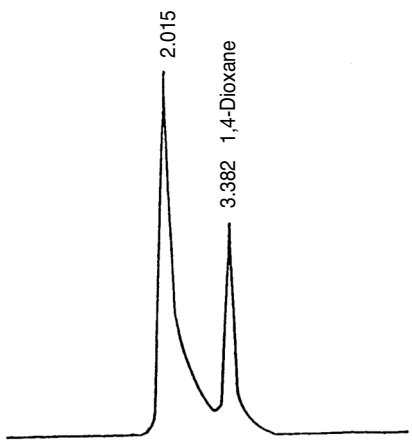

Figure 2. 1,4-Dioxane (2.5 ppm) in water on an OV-351 column.

Results and Discussion

Glycols and 1,4-dioxane are better analyzed on polar phases such as Carbowax 20M or OV-351 when they are present together. Yancey (4,5) has reported that polyethylene glycol (PEG) is the second most popular GC phase (showing a wide

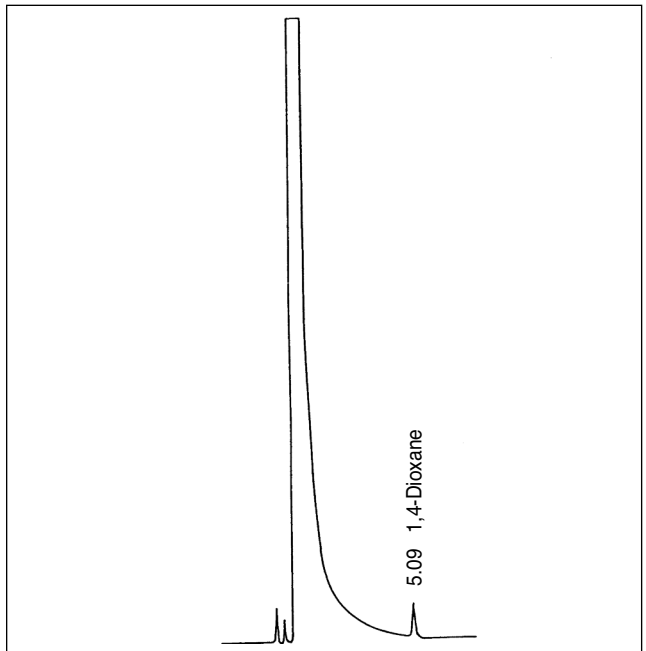

Figure 3. 1,4-Dioxane (2.5 ppm) in MeOH on a BP 20 capillary column.

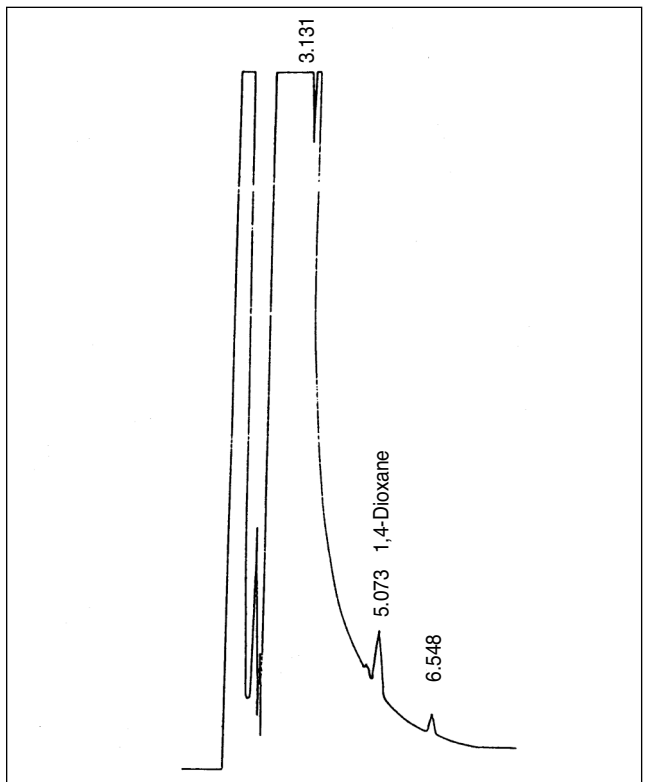

Figure 4. 1,4-Dioxane (2.5 ppm) in benzene on a BP 20 capillary column.

range of moderate selective interactions) and is useful for the general GC analysis of organic compounds. Hydrogen bonding is the major selective interaction for this phase, and glycols by virtue of the presence of hydroxyl groups would be retained for a longer time than 1,4-dioxane (the cyclic ether, which is nonpolar) giving good separation. On the OV-351 column, the RT of 1,4-dioxane was approximately 3.4 min (i.e., it was retained for a relatively longer time than on the Carbowax 20M column). The OV-351 phase is more polar and can give rise to dipole–induced dipole attractions for 1,4-dioxane, which itself has no dipole but has polarisable electrons (heteroatoms) resulting in more retentiveness on the OV-351 phase. The linearity of the aqueous solutions of 1,4-dioxane on both of the packed columns was good (Figure 5). These results show that packed columns can be used for the analysis of 1,4-dioxane in glycol samples diluted with water. However, the polar stationary phases such as Carbowax and OV-351 are susceptible to deterioration in the analysis of an aqueous sample because of water and oxygen in the carrier gas (6). Injecting a large number of aqueous samples may therefore affect the column performance. In view of this, the BP 20 capillary column (equivalent to Carbowax 20M) was used for the analysis of 1,4-dioxane in water, methanol, and benzene. The PEG capillary columns also need to be protected from adventitious air and water in order to avoid deterioration (5). SGE (7) recommends the use of deactivated capillary tubing in order to overcome the problem of aqueous sample injections. Methanol solutions of 1,4-dioxane could therefore be analyzed without the use of deactivated tubing in order to avoid the problem of aqueous sample injections. Glycols are viscous liquids that have boiling points at approximately 200°C and above. Neat injections of glycols in a GC pose problems and require high injection-port temperatures. Dilutions with methanol help reduce the viscosity of the sample and also ensure homogeneity; therefore, 5- and 2.5-ppm solutions of 1,4-dioxane in 50% ethylene glycol and 50% methanol were analyzed. This analysis was carried out using injection-port temperatures at 200°C and 230°C while keeping all the other analytical conditions the same. It was observed that an increase in the injection-port temperature of the glycol sample that was diluted with methanol containing 2.5 ppm of 1,4-dioxane resulted in an increase in the area count of 1,4-dioxane. As a result, it became almost equal to that of the 2.5-ppm sample in methanol only. This observation shows that it is necessary to dilute the glycol sample and use a high injection-port temperature to ensure detection at low levels. Typical chromatograms are shown in Figures 3 and 6.

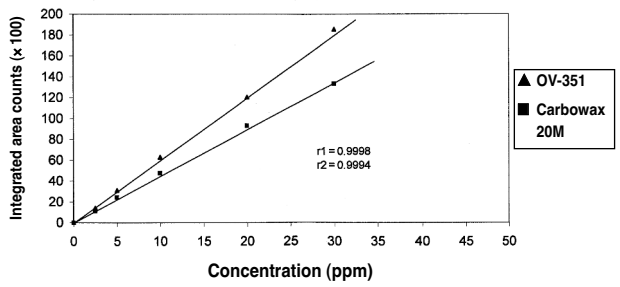

Figure 5. Linearity of 1,4-dioxane in water on OV-351 and Carbowax 20M packed columns.

Figure 6. 1,4-Dioxane (2.5 ppm) in MeOH–ethylene glycol (50:50) on a BP 20 capillary column with the injection-port temperature increased to 230°C.

The determination of 1,4-dioxane in benzene was carried out on a capillary column. A distinct peak of 2.5-ppm 1,4-dioxane at an RT of approximately 5 min was observed even though it is on the tail of benzene. In this case, it is not necessary to temperature-program the oven, because the analysis was carried out at an oven temperature of 70°C. The linearity of 1,4-dioxane solutions in methanol as well as benzene was good (Figure 7). The substantial difference in the area counts for the identical concentrations of 1,4-

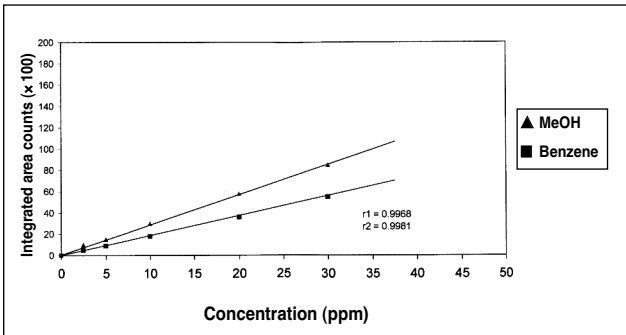

Figure 7. Correlation between the peak area and the concentration of 1,4-dioxane on a BP 20 capillary column.

dioxane may be attributed to the fact that in the case of benzene, the 1,4-dioxane peak is on the tail, and in the case of methanol, it is distinctly separated.

Conclusion

1,4-Dioxane at low parts-per-million levels (up to 2 ppm) can be determined in glycols using packed as well as capillary columns. Because the stationary phases are likely to be deteriorated by injecting aqueous samples, glycols are preferably diluted with methanol instead of water.

References

1. *Merck Index*, 12th ed. S. Budhavari, Ed. Merck & Co., Whitehouse Station, NJ, 1996, p 8358.
2. *DOW Glycols*. The Dow Chemical Company, p 14.
3. R.L. Grob. *Standard Practice of Gas Chromatography*, 2nd ed. John Wiley & Sons, New York, NY, 1985, p 701.
4. J.A. Yancey. Review of liquid phases in gas chromatography. Part I. Intermolecular forces. *J. Chromatogr. Sci.* **32:** 349–57 (1994).
5. J.A. Yancey. Review of liquid phases in gas chromatography. Part II: Applications. *J. Chromatogr. Sci.* **32:** 403–11 (1994).
6. R.L. Grob. *Standard Practice of Gas Chromatography*, 2nd ed. John Wiley & Sons, New York, NY, 1985, p 156.
7. Products 98/99. In *SGE Catalogue of Chromatography*. SGE, Ringwood Victoria, Australia, p 123.

Manuscript accepted October 23, 2000.