Gas Chromatographic Determination of 1,4-Dioxane in Benzene

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Received:04 December 2000; accepted: 01 February 2001

The term 'petrochemicals' implies the basic chemicals derived from refinery petroleum cuts. They are produced by the separation of the byproducts from the cracking of hydrocarbon streams. The basic petrochemicals, which are produced in large volumes, are divided into two classes: olefins and aromatics. Olefins include ethylene, propylene and 1,3-butadiene. Aromatics such as benzene, toluene and xylenes are obtained from refinery and petrochemical light naphtha streams. Aromatics are produced in the reforming process and in steam cracking. Extraction or various extractive distillation processes are used to isolate and separate aromatics from the naphtha streams. Typical extraction processes are based on tetra-ethylene glycol, sulpholane, N,N'-methyl pyrrolidone or morpholine. They produce a mixture of aromatics that are subsequently separated by distillation. Glycols in extraction processes contain small amounts of 1,4-dioxane, which gets distilled over with benzene when aromatics are separated by distillation. In view of the hazardous properties, it is necessary to determine the levels of 1,4-dioxane in glycols and benzene. Determination of 1,4-dioxane in glycols at low ppb levels has already been reported. The detailed studies carried out for the gas chromatographic determination of 1,4-dioxane in benzene including column selection and linearity are reported in the present communication.

Introduction

Compound 1,4-dioxane is a flammable liquid having pleasant odour. Its vapours are harmful and it tends to form explosive peroxides. 1,4-dioxane is present in glycols which are used in the extraction processes to isolate and separate aromatics from the naphtha streams and it eventually gets distilled over with the benzene in the distillation process. 1,4-dioxane is cyclic ether and non-polar. Because of the low reactivity of the functional group the chemical behaviour of ethers both aliphatic and aromatic, resembles that of hydrocarbons to which they are related. Qualitative identification and quantitative determination of small amounts of 1,4-dioxane in benzene is difficult by conventional methods because of its inert nature. Gas chromatography is the convenient technique for the purpose of achieving separation and detection of 1,4-dioxane in benzene. So far no work is reported in literature on 1,4-dioxane other than the determination of 1,4-dioxane at low ppb levels in glycols.

Materials and Methods

Chemicals Used

1,4-dioxane - HPLC grade was obtained from Qualigens (A division of Glaxo) and Benzene - HPLC grade was obtained from Qualigens (A division of Glaxo).

GC Analysis

Gas chromatographic studies were carried out using CHEMITO 8610 gas chromatograph having one packed and one capillary port with Flame Ionization Detector (FID). CHEMITO C-5000 Data Processor was used for data handling.

The packed columns and capillary columns used in the present studies were:

(i) 5 per cent Carbowax 20 M on 80/100 mesh, Chromosorb W (HP), 2 m X 3 mm OD SS.
(ii) 10 per cent OV-351 on 80/100 mesh, Chromosorb W (HP), 2 m X 3 mm OD SS.
(iii) 25 per cent TCEP on 80/100 mesh, Chromosorb W (HP), 2.5 m X 3 mm OD SS.

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(iv) Capillary column BP 20, 25 m length, 0.32 mm ID, 1.0 μm film thickness.
(v) Capillary column BP 21, 25 m length, 0.32 mm ID, 0.5 μm film thickness.
(vi) Wide bore capillary column BP 624, 30 m length, 0.53 mm ID, 3.0 μm film thickness.

The capillary columns were obtained from SGE, Australia.

Analytical Conditions

The analytical conditions set for the analysis were:

(i) 5 per cent Carbowax 20M column, Carrier gas - Nitrogen, 30 mL/min. Injection port temperature - 200°C, Oven temperature - 40°C, Detector temperature - 200°C, Range X1, Injection volume - 1 μL.

(ii) 10 per cent OV 351 Column, Carrier gas - Nitrogen, 30 mL/min. Injection port temperature - 150°C, Oven temperature - 80°C hold for 5 min @ 3°C/min to 120°C, Detector temperature - 150°C, Range X10, Injection volume - 1 μL.

(iii) 25 per cent TCEP Column, Carrier gas - Nitrogen, 30 mL/min. Injection port temperature - 150°C, Oven temperature - 80°C, Detector temperature - 150°C, Range X10, Injection volume - 1 μL.

(iv) Capillary column BP 20, Carrier gas - Nitrogen, Head pressure - 1.4 bar, Makeup gas - Nitrogen - 1.4 bar, Injection port temperature - 150°C, Oven temperature - 70°C, Detector temperature - 150°C, Split - 15 mL/min, Purge - 1 mL/min, Range X1, Injection volume - 0.5 μL.

(v) Capillary column BP 21, Carrier gas - Nitrogen, Head pressure - 1.2 bar, Makeup gas - Nitrogen - 1.4 bar, Injection port temperature - 150°C, Oven temperature - 45°C, Detector temperature - 150°C, Split - 15 mL/min, Purge - 1 mL/min, Range - X10, Injection volume - 1 μL.

(vi) Wide bore capillary column BP 624, Carrier gas nitrogen - 5 mL/min. Makeup gas - Nitrogen, Head pressure - 1.4 bar, Makeup gas - Nitrogen - 1.4 bar, Injection port temperature - 150°C, Oven temperature - 70°C, Detector temperature - 150°C, Split - 15 mL/min, Purge - 1 mL/min, Range X1, Injection volume - 0.5 μL.
Solution Preparation

Solutions of 1.0, 2.0, 2.5, 5.0, 10.0, 20.0, and 30.0 ppm of 1,4-dioxane in benzene were freshly prepared for each analysis.

1,4-dioxane solution of 5 ppm was analyzed on Carbowax 20M, OV-351 and TCEP columns under the conditions described above. The retention time (RT) of 1,4-dioxane and benzene was about 3.7 min and 3.3 min, 7.1 min and 4.1 min and 16.2 and 8.5 min respectively. 1,4-dioxane solution of 2.5 and 2 ppm was analyzed on Capillary columns BP 20, BP 21 and BP 624 also. The RT of 1,4-dioxane and benzene was about 5.0 min and 3.0 min, 3.3 min and 1.6 min and 20 min and 12 min, respectively. The linearity of 1,4-dioxane on capillary column BP 20 is good although the peak appears on the tail of benzene. The typical chromatograms and the linearity graph are shown in the Figures 1-3.

Results and Discussion

In gas chromatographic analysis, the choice of the liquid phase depends on the composition of the sample. When the components of the mixture are of different chemical classes, as is the case with benzene, an aromatic hydrocarbon and 1,4-dioxane a cyclic ether, one has to try liquid phases of different polarities to achieve the separation of the two components present in the mixture particularly when one of them is present at ppm levels vis-à-vis very large concentration of the other constituent. In such cases the resolution of chromatographic peaks, which depends on column efficiency and choice of the liquid phase becomes significant. The packed columns used in the present studies resolve benzene and 1,4-dioxane. However, the concentration of benzene is too high as compared to 1,4-dioxane and therefore 1,4-dioxane appears on the tail of benzene, when the sensitivity is increased to detect 1,4-dioxane at low ppm levels. The 1,4-dioxane peak either gets masked or goes undetected because of large broadening of the benzene peak. The analysis was therefore attempted on capillary columns of various polarities. On capillary column BP 20, benzene and 1,4-dioxane show good separation. The separation is achieved because the liquid phase BP 20, i.e., Carbowax 20M is polar and induces small dipole in benzene by polarizing its π-electron cloud while in the case of 1,4-dioxane, dipole-induced dipole attractions come into play as 1,4-dioxane has no dipole but has polarizable electrons (heteroatoms) which result in more retentivity vis-à-vis benzene on Carbowax 20M phase. In addition the boiling point difference between benzene (80°C) and 1,4-dioxane (101°C) may also assist in separation of 1,4-dioxane in benzene.

The RT of 1,4-dioxane and benzene on BP 21 capillary column is around 3.3 min and 1.6 min, respectively but the 1,4-dioxane peak is on the tail of benzene and it becomes difficult to quantitatively estimate 1,4-dioxane.
The capillary column BP 624 is 6 per cent cyanopropyl phenyl - 94 per cent dimethyl polysiloxane phase and is used for the analysis of various solvents including benzene and 1,4-dioxane. The cyano group has the strongest dipole of all the functional groups contained in stationary phases used in capillary columns and its selectivity is caused by dipole-dipole or induced-dipole interactions. This selectivity being similar to BP 20 (Carbowax 20M) phase and it was tried for the analysis of 1,4-dioxane in benzene. Benzene produced a complex chromatogram (Figure 2) on BP 624 column because of the resolution of associated impurities. Depending on the nature of associated impurities in benzene and their relative concentrations, it may be possible that 1,4-dioxane peak gets masked at high sensitivity settings. Therefore, it is preferable to use BP 20 capillary column for routine determination of 1,4-dioxane in benzene. The BP 624 capillary column may be used after ascertaining that the peak of 1,4-dioxane is distinctly separated from the associated impurities of benzene.

**Conclusion**

1,4-dioxane at low ppm levels in benzene can be detected using BP 20 capillary column. Even though the 1,4-dioxane peak is on the tail of benzene, it is reproducible and shows good linearity in the working range of interest.

**References**