Purity Analysis of Industrial Triethylene Glycol by Capillary Gas Chromatography

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Abstract

The Daqing Petrochemical Complex has established a new, accurate method for the analysis of industrial triethylene glycol based on capillary gas chromatography. With this new method, it is now possible to identify the tetrapropylene glycol content, which in previous methods appeared in the main peak of triethylene glycol.

Introduction

Triethylene glycol (TEG) is an organic chemical product synthesized by ethylene oxidation with air over a silver catalyst, forming ethylene oxide polymers, followed by hydrolysis. It is used as a solvent in resins and gums, as raw material for producing various TEG derivatives, and also widely used in organic synthesis.

For the purity analysis of industrial TEG, the Occidental Chemical Corporation (OCC) used two methods: distillation (initial boiling point and final boiling point) and gas chromatography (GC). When GC was used, there was always an inseparable shoulder peak on the main peak of TEG (1). The unknown shoulder peak has now been identified as tetrapropylene glycol. Because these peaks were originally not well separated, the accuracy of the analysis result was not satisfactory. This was a problem in the commodity inspection of the imported TEG for many years. GC is now the standard method used in the determination of the TEG purity. To our knowledge, results of TEG purity analysis by capillary GC have not previously been reported in the literature.
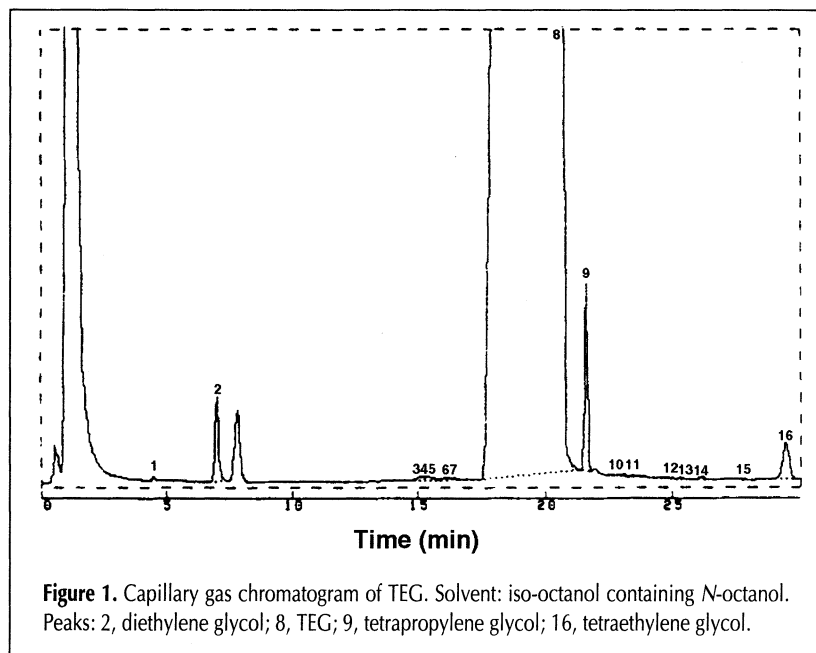
Experiment

Instruments and operating conditions

The GC used was a Shimadzu (Kyoto, Japan) model GC-16A equipped with a flame-ionization detector (FID), a model AOC-9 auto sampler, a model C-R4A Chromatopac data processor, a model OPGU-500s hydrogen generator, and a Hitachi (Tokyo, Japan) model 0.20P-5s air compressor. The column was a PEG-20M fused quartz capillary (12 m × 0.53-mm i.d., 1.0-µm film-thickness) (Scientific Glass Engineering, Victoria, Australia). The carrier gas was high-purity helium (BAIF, Beijing, China) at a velocity of 6.62 mL/min (25 kPa), and the makeup gas was helium at 20 mL/min. The temperature was programmed at 135°C (held for 8 min) and increased at 3°C/min to 180°C (held for 9 min).

For GC–MS, a Hewlett-Packard (Avondale, CA) 5890 series II GC/5971A MSD was used. The column was an FFAP fused-silica capillary (30 m

Figure 1. Capillary gas chromatogram of TEG. Solvent: iso-octanol containing *N*-octanol. Peaks: 2, diethylene glycol; 8, TEG; 9, tetrapropylene glycol; 16, tetraethylene glycol.

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Table I. Qualitative Analysis Results of the Impurities Present in Industrial TEG

Peak*	Molecular weight	Formula	Name
2	106.12	$C_4H_{10}O_3$	diethylene glycol
8	150.17	$C_6H_{14}O_4$	triethylene glycol
9	250.33	$C_{12}H_{26}O_5$	tetrapropylene glycol
14	194.23	$C_8H_{18}O_5$	tetraethylene glycol

* Corresponding to the peak number in Figure 1.

Table II. Comparison of Physical Constants of Glycols*

Name	Molecular weight	Melting point (°C)	Boiling point (°C)	Flash point (°C)
Propylene glycol	76.1	–60	188	107
Ethylene glycol	62.07	–13/–12.6	197.6/197.3	110
Dipropylene glycol	134.18		231.8	138
Diethylene glycol	106.12	–10.45	245	143
Tripropylene glycol	192.3		267.2	141
TEG	150.17	–7.2/–4.3	285	166/165
Tetrapropylene glycol	250.33			
Tetraethylene glycol	194.23	–6	307.8	176

* *Lange's Handbook of Chemistry* (2) did not include the physical constants of tetrapropylene glycol such as boiling point, etc. Its boiling point was inferred to be slightly greater than that of triethylene glycol.

Table III. Precision of the Triethylene Glycol Analyzed by the DPC Method (%)

Sample 1 Analysis	DEG	TEG	TetraPG	TetraEG
1	0.114	99.606	0.198	0.082
2	0.114	99.603	0.198	0.084
3	0.114	99.604	0.198	0.084
4	0.114	99.602	0.199	0.084
5	0.114	99.603	0.197	0.085
6	0.114	99.603	0.198	0.085
7	0.114	99.602	0.198	0.085
8	0.114	99.602	0.199	0.082
Average	0.114	99.603	0.198	0.085
Relative standard deviation	0	0.001	0.32	1.23

Sample 2 Analysis	DEG	TEG	TetraPG	TetraEG
1	0.124	99.583	0.215	0.078
2	0.122	99.584	0.216	0.077
3	0.124	99.581	0.218	0.077
4	0.124	99.581	0.219	0.077
5	0.123	99.582	0.219	0.077
6	0.123	99.585	0.216	0.076
7	0.123	99.583	0.218	0.076
8	0.124	99.582	0.219	0.075
Average	0.123	99.583	0.218	0.077
Relative standard deviation	0.60	0.001	0.74	1.2

× 0.53-mm i.d., 1.0-μm film), and high-purity helium (70 kPa) was used as the carrier gas. The temperature was programmed at 60°C and increased 10°C/min to 220°C. Electron-impact (EI) ionization was employed; the mass range was 10–310 amu, and the scan parameter was 3A/D at 1.4 full scans/s.

Procedures

A 1.5-mL volume of iso-octanol chromatographic solvent (Tianjin Chemical Reagent Factory No. 2, Tianjin, China) that was well-separated from the glycolic sample components was used to dilute 0.5 mL of TEG sample. With a clean, dry 10-μL micro syringe, a 1-μL diluted sample of industrial TEG was injected to perform GC analysis. The area normalization method was used for the calculation.

Results and Discussion

Qualitative analysis of impurities

Under the above-mentioned GC–MS conditions for analysis of imported industrial TEG, the total ion chromatgram (TIC) was obtained. By individually and qualitatively analyzing the peaks in the TIC, it was found that they came out basically in order of carbon number, but due to the difference in molecular structure, some individual components appeared in other carbon distribution areas. The results of the MS analysis are shown in Table I.

Physical constant discussion

From Table I, it is clear that peak 9 was tetrapropylene glycol. Although tetrapropylene glycol has a different molecular structure and weight than TEG, its physical properties are close to those of TEG, which is due to the difference in molecular structure. For comparison, the relevant physical constants of some glycols are listed in Table II.

Selection of GC conditions

Analysis of TEG was initially carried out in a 2-m × 3-mm-i.d. PEG-20M glass packed column (Shimadzu, Kyoto, Japan). However, it was not possible to separate the back shoulder peak of tetrapropylene glycol from the main peak of TEG, and the analysis time was too long. This was mainly because the packed column had a lower number of theoretical plates and low efficiency, so it was hard to separate components with similar physical and chemical properties. In a 25-m × 0.2-mm-i.d. PEG-20M fused-quartz capillary column, the back shoulder peak of tetrapropylene glycol was well-separated from the main peak of TEG because of the split injection mode, but quantitative analysis was a rather

Table IV. Comparison of TEG Results (%) Obtained by Different Methods

Sample 1	DPC method	OCC method*
TEG	99.603[†]	99.70
Diethylene glycol	0.114	
Tetraethylene glycol	0.084	
Tetraproplyne glycol	0.198	
Total Diethylene glycol + tetraethylene glycol	0.198	0.19
Total organic impurities	0.396	0.19
Water	0.050	0.09

Sample 2	DPC method	OCC method*
TEG	99.583[†]	99.70
Diethylene glycol	0.123	
Tetraethylene glycol	0.077	
Tetraproplyne glycol	0.218	
Total Diethylene glycol + tetraethylene glycol	0.200	0.19
Total organic impurities	0.418	0.19
Water	0.054	0.09

* Contract specifications provided by OCC: TEG ≥ 99.5%; other glycols ≤ 1.0%; H_2O ≤ 0.1%; initial boiling point, 278°C; final boiling point, 300°C (760 mm Hg).
[†] Water-free basis.

complex and difficult task. With a 12-m × 0.53-mm-i.d. PEG-20M fused-quartz capillary column, the separation between TEG and tetrapropylene glycol was very much improved, and the detection sensitivity was higher because the sample injection mode was controlled by a constant flow. The sample was directly flashed in the injection port and in a splitless mode. The excellent results achieved on the 12-m × 0.53-mm-i.d. PEG-20M fused-quartz capillary column were due to the fact that it had the advantages of both a packed column and a capillary column (i.e., the sample capacity was similar to that of the packed column, but it still possessed the high resolution efficiency of the capillary column). This column was simple, easy to operate, precise, and accurate for quantitative analysis, and the analysis time was reasonably short. The analysis of one sample typically took 30 min. A typical chromatogram is shown in Figure 1.

Precision and accuracy

From the qualitative analysis results, it was clear that the impurity had a molecular structure similar to that of the main component. Based on past research of the author from the Daqing Petrochemical Complex (DPC) (3), it was considered that the correction factor was similar. Because the impurity was very minor, the area normalization method could be used to calculate the result. The results of this analysis are shown in Table III.

Method comparison

Two TEG samples were analyzed by both the OCC and DPC for impurities. The results of these analyses are shown in Table IV. From these results, it is clear that the tetrapropylene glycol content, which had previously been included in TEG, could now be identified with the DPC method.

Conclusion

DPC has identified the unknown component that formed an unknown shoulder on the main peak of TEG. This component was identified as tetrapropylene glycol, and the uncertainty as to the qualitative and quantitative analysis of TEG was resolved. This new GC–MS method was very simple and accurate, and it met all accuracy requirements for the commodity inspection of imported industrial TEG.

References

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