CHROM. 18 872

Note

Gas chromatographic determination of dimethyl ether in a mixture containing propane, C$_4$ hydrocarbons, *n*-pentane, methyl *tert.*-butyl ether and methanol

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(First received March 19th, 1986; revised manuscript received June 13th, 1986)

The reduction of lead use in gasoline mandated by the U.S. Environmental Protection Agency has greatly increased the demand for both methyl *tert.*-butyl ether (MTBE) and other octane boosters. Since then MTBE production has grown quickly and output totaled 1.5 · 10^9 of lbs. in 1984[1]. During MTBE synthesis, a trace amount of dimethyl ether (DME) may be formed. Since DME decomposition leads to polymer formation, the presence of DME could impact refinery operation. Thus, precise determination of DME concentration is needed. A number of gas chromatographic (GC) procedures have been reported in the literature for DME analysis. Stockinger[2] used (1) a column (2.4 m × 3.2 mm O.D.) packed with Porapak Q (80–100 mesh) with nitrogen and helium as the carrier gas with a thermal conductivity detector; and (2) a support (squalane)-coated open-tubular column (61 m × 0.8 mm O.D. × 0.5 mm I.D.) with helium as the carrier gas and flame ionization detector. Hayashi and Moffat[3] separated methanol, DME, carbon monoxide, carbon dioxide and C$_1$–C$_3$ hydrocarbons on a Porapak Q column (3 m × 6.4 mm O.D.) at 70°C. Muja and co-workers[4] used a C$_{22}$ Celite column (5 ft. long) packed with 19% tri(cyanoethoxy)propane for detecting DME in the reaction mixture from MTBE synthesis. However, the DME peak as reported in the literature[1,2] is closely adjacent to methanol or C$_4$ fractions. Thus, it is difficult to determine small DME concentrations when methanol or C$_4$ fractions are present[2]. This paper describes a DME analysis using a column packed with Porapak N/Q (Porapak N–Porapak Q, 80:20).

EXPERIMENTAL

Apparatus
The column used in this study was a stainless-steel column (2.4 m × 3.2 mm O.D.) packed with Porapak N (80%) and Porapak Q (20%) purchased from Carle Instruments (Anaheim, CA, U.S.A.). The column was conditioned at 170°C overnight with nitrogen as the carrier gas before use. The GC instrument used in our laboratory was a Varian Model 3700 equipped with a flame ionization detector, recording integrator (Varian Model CDS-111) and temperature programming. The column temperature started at 40°C for 12 min, then slowly increased to 170°C at a rate of 4°C/min, and was held at 170°C for 13 min. Nitrogen was used as the carrier

gas at a rate of 30 ml/min. The injector and detector temperatures were set at 150°C and 200°C, respectively.

DME analysis

Standards were prepared as follows. First, the DME standards were prepared by injecting 0.1, 0.25, 0.5, 0.75 and 1.0 ml of DME gas at atmospheric pressure into 125-ml serum bottles. A second set of DME standards were prepared by filling a gas sample with 3 p.s.i.g. of tank gas containing propane, methanol, isobutylene, iso-butane, *n*-butane and *n*-pentane (Table I), followed by injecting 0.1, 0.25, 0.5, 0.75 and 1.0 ml of DME gas to the bottles. A third standard was prepared by injecting 0.1 ml of MTBE into the second set of DME standards. In both cases, three to four replicate samples were injected for each standard. Table II provides a guide to gas composition ranges for standards I, II and III prepared with 0.1 ml DME gas injected into the 125-ml serum bottles.

RESULTS AND DISCUSSION

For DME alone a retention time of 22.71 min was determined. For DME in a mixture with tank gas, a retention time of 22.71 min for DME and 27.05 min for methanol was measured. The DME peak is well separated from the propane, meth-anol and C_4 fractions, although the methanol peak can be overshadowed by the C_4 fractions as shown in Fig. 1. These 5 min between the DME and methanol peaks make it possible to detect concentrations of DME as low as 50–100 ppm in a large sample size.

Both the calibration curves based on a replicate of three to four samples for each DME concentration indicated a good correlation between the peak area and the DME concentration. The correlation coefficients are calculated as 0.9927 and 0.9838, respectively, as shown in Figs. 2 and 3. Thus, peak area instead of peak height was used in all runs. The mixture containing 0.1 ml of MTBE in DME standard II showed a retention time of 44.03 min for MTBE (Fig. 4). The calibration curve obtained with MTBE addition is the same as that in standard II. This shows that one sample run will take about 50 min before the second sample can be injected.

The procedure developed in this study has been tested for a period of two months and reproducible data were consistently obtained.

TABLE I

ANALYSIS OF TANK GASES

Analyzed by Matheson Gas Products, Inc.

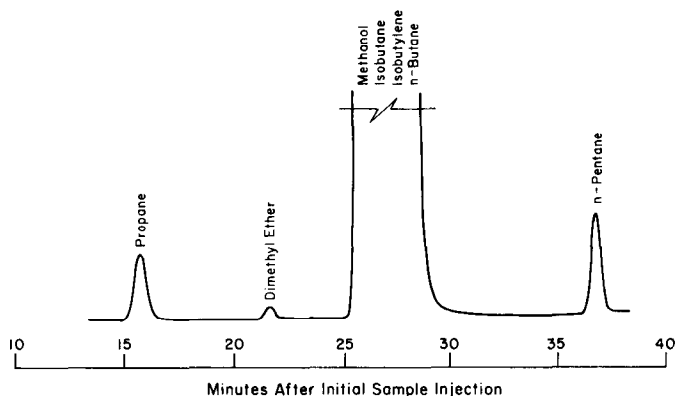| Compound	Percentage (w/w)
Propane	0.476
Methanol	10.69
Isobutane	35.27
Isobutylene	18.36
n-Butane	34.72
n-Pentane	0.484

Fig. 1. Typical chromatogram of DME in a mixture with methanol, propane, C_4 fractions and n-pentane using flame ionization detection. Column: 2.4 m × 3.2 mm O.D. Porapak N/Q. Temperature: 40°C for 12 min, then programmed at 4°C/min to 170°C, hold for 13 min. Carrier gas: nitrogen at 30 ml/min. Sample size: 50 μl.
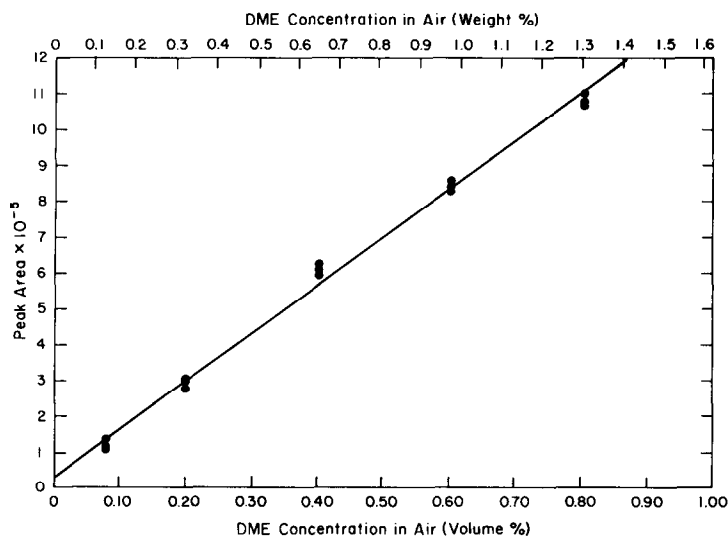

Fig. 2. Calibration curve for the DME standard I. Sample size was 50 μl. Calibration curve given by $Y = 1\ 343\ 000\ X + 30\ 640$ with a correlation coefficient of $r = 0.9972$.

CONCLUSIONS

A GC column packed with Porapak N/Q (Porapak N–Porapak Q, 80:20) was used for analyzing DME in a mixture containing propane, DME, methanol, C_4 fractions, n-pentane and MTBE with a flame ionization detector and temperature programming. Nitrogen was used as the carrier gas. The retention time for propane, DME, methanol, C_4-fractions, n-pentane and MTBE were 16.86, 22.71, 27.05, 28.87, 37.87 and 43.96 min, respectively. With a sample size of 50 μl, DME levels on the

TABLE II

COMPOSITION OF GAS STANDARDS

Components	Standard I		Standard II		Standard III	
	Weight (%)	Mole (%)	Weight (%)	Mole (%)	Weight (%)	Mole (%)
Propane**	—	—	0.55	0.70	0.53	0.68
n-Butane**	—	—	37.47	35.75	35.90	34.79
Isobutane**	—	—	37.01	35.31	35.46	34.36
Isobutylene***	—	—	19.58	19.35	18.76	18.84
Methanol***	—	—	4.91	8.50	4.70	8.27
n-Pentane**	—	—	0.42	0.32	0.40	0.31
DME	0.13	0.08	0.06	0.07	0.06	0.07
MTBE***	—	—	—	—	4.19	2.68
Nitrogen	78.90	81.06	—	—	—	—
Oxygen	20.97	18.86	—	—	—	—

* Based on calculations for flash vaporization process.
** The equilibrium distribution coefficient was obtained from ref. 5.
*** The equilibrium distribution coefficient is approximated as P_{vap}/P, where P_{vap} is the vapor pressure and P is the total pressure.
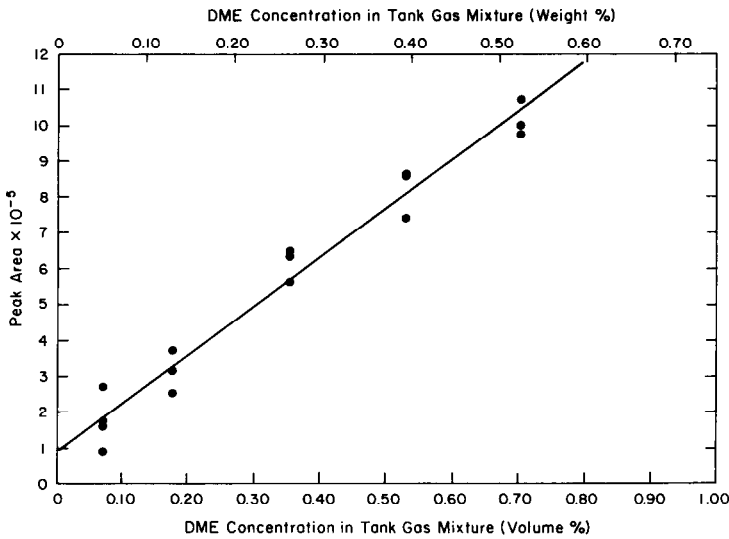
Fig. 3. Calibration curve for the DME standard I in a mixture with tank gases (DME standard II). Sample size was 50 μl. Calibration curve given by $Y = 1\ 369\ 000\ X + 88\ 520$ with a correlation coefficient of $r = 0.9838$.
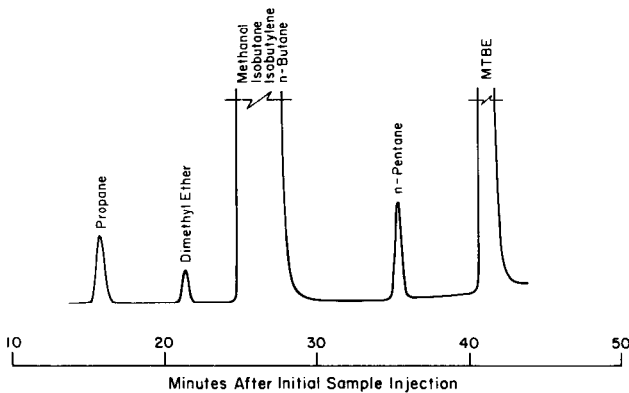

Fig. 4. Typical chromatogram of DME (0.75 ml) in a mixture with propane, methanol, C$_4$-fractions, n-pentane and MTBE (DME standard III). Sample size was 50 μl.

order of 1000 ppm were readily quantitated. The 5-min difference in retention time between the DME and methanol peaks made it possible directly to quantitate DME in the 50- to 100-ppm concentration range for a sample size of 500–1000 μl. This analytical procedure has been tested and reproducible data were consistently obtained.

ACKNOWLEDGEMENT

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