# Note

## Direct gas chromatographic determination of alcohols and methyl *tert.*-butyl ether in gasolines using infrared detection

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The improvement in gasoline octane rating by addition of oxygenated compounds has received considerable attention recently. Lower alcohols are commonly used, *e.g.* methanol, ethanol, propan-2-ol and *tert.*-butanol as well as methyl *tert.*-butyl ether (MTBE). These are added at the low percent level.

There is a need for methods of analysis for such additives and several have been described. Alcohols may be isolated from gasolines by aqueous extraction and subsequent injection into a gas chromatograph which has a flame ionisation detector. MTBE and isopropanol may be separated by adsorption on silica gel followed by desorption with methanol and subsequent gas chromatographic (GC) determination[1]. Reversed-phase liquid chromatography followed by refractometer detection has given good results but requires purging of the column with acetonitrile for 5 min to remove gasoline residues before any further sample can be injected[1]. Other workers have used gas chromatography with a column switching procedure[2].

The combination of the separating power of GC with the selective detection of an infrared detector appeared to give a promising basis for the rapid analysis of these samples without any need for sample pretreatment. This report describes the development and evaluation of such a method.

EXPERIMENTAL

A Sigma 2 gas chromatograph (Perkin-Elmer) fitted with a flame ionisation detector was used with a 3 ft. × 1/8 in. O.D. column (stainless steel) packed with Porapak Q or with a 1:1 mixture of Porapak Q plus Porapak N (Waters Assoc.). Column temperature was 175°C and helium was used as carrier gas (8 ml/min).

The new Miran infrared GC detector was used as the selective detector with a standard 0.5-ml cell as recommended for use with packed columns. The cell was fitted with zinc selenide windows. Flexible metal capillary lines were used to connect the outlet of the column to the infrared detector cell and also to connect the detector cell outlet to the normal inlet of the flame ionisation detector. The outputs of the two detectors were displayed on a dual-pen recorder (Model R12, Rikadenki Corporation).

The infrared detector cell, and connecting capillary lines were maintained at 175°C. Slit width was 2 mm and response time was set to 40. Absorbance ranges were

0.025 to 0.25. Alcohols were monitored at 9.25 $\mu$m and MTBE at 8.3 $\mu$m unless otherwise stated.

Standard solutions of alcohols were prepared in water (0.1% to 20%, w/v) for initial measurement of detector linear range. Similar solutions were prepared in alcohol-free gasoline for quantitative analysis of samples.

MTBE standards were prepared in ethanol or gasoline (0.25% to 4%, w/v). Sample size was 1 $\mu$l. Peak height measurements were used for quantitative work.

RESULTS AND DISCUSSION

Separation of most of the alcohols and MTBE was achieved in 10 min using the Porapak Q column. Relative retention data are given in Table I. The use of a short column has given a moderate plate count but separation of the alcohols of interest is well defined. The separation of *sec.*-butanol and MTBE however is unsatisfactory. Although a range of packed columns was tried complete separation of the six components was not achieved with a fast analysis time and a suitable flow-rate for optimum infrared sensitivity. However a 1:1 blend of Poropak Q and Poropak N gave the required separation (Fig. 1) with the relative retention times also given in Table I.

The flame ionisation detector was used only for initially setting up the separation. The response of the two detectors are compared in Fig. 2. The flame ionisation detector shows that the early peaks would interfere with some of the alcohol peaks. The infrared detector shows only the peaks of the oxygenated compounds. The later gasoline peaks give no response at all.

The detector sensitivity was greater at low volume flow-rates and 8 ml/min gave a reasonable compromise between good sensitivity, reasonable analysis time and column efficiency.

The sensitivity of the detector to alcohols would clearly be dependent on the precise monitoring wavelength. The maximum of absorbance of the characteristic C–O–H stretch decreases from 9.5 $\mu$m to 8.2 $\mu$m with change from primary to secondary to tertiary alcohols[3]. Analysis of an unknown mixture therefore required the use of a compromise wavelength (9.25 $\mu$m).

The appearance of the chromatogram for alcohols is shown to change dramatically with change of monitoring wavelength (Fig. 3).

The limits of detection of the compounds at different wavelengths are shown

TABLE I

RELATIVE RETENTION TIMES FOR ALCOHOLS AND MTBE

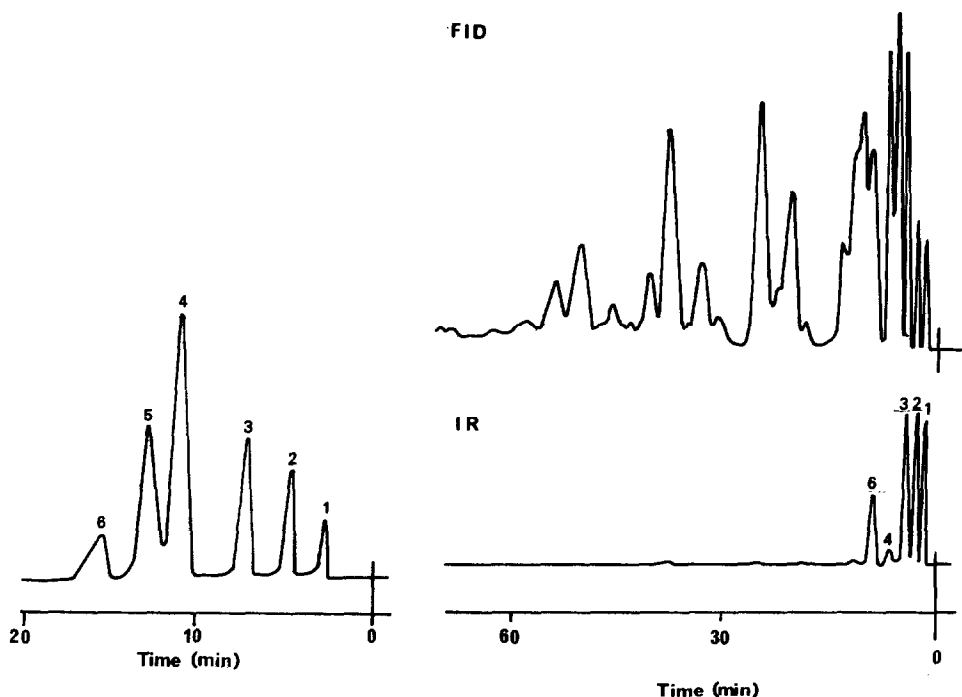|  | Porapak Q 175°C | Porapaks Q + N 175°C |
| --- | --- | --- |
| Methanol | 0.28 | 0.21 |
| Ethanol | 0.59 | 0.55 |
| Propan-2-ol | 1.00 | 1.00 |
| *tert.*-Butanol | 1.61 | 1.64 |
| *sec.*-Butanol | 2.29 | 2.52 |
| MTBE | 2.46 | 2.00 |

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Fig. 1. Separation of alcohols and MTBE on Porapak Q/N at 175°C. Peak elution order: 1 = methanol, 2 = ethanol, 3 = propan-2-ol, 4 = *tert.*-butanol, 5 = MTBE, 6 = *sec.*-butanol.

Fig. 2. Comparison of flame ionisation and infrared response for gasoline containing alcohols. Porapak Q, 175°C, infrared detection at 9.25 $\mu$m. Peak numbers as in Fig. 1.

in Table II. The linearity of response of the infrared detector was excellent over the ranges 0–2% w/v (methanol and ethanol), 0–3% (*tert.*- and *sec.*-butanol), 0–4% for propan-2-ol and 0–2.5% (MTBE).

MTBE had a strong C–O–C stretch absorbance at 8.3 $\mu$m which was similar to that for alcohols. Using the Porapak Q column, where MTBE had a similar re-

TABLE II

LIMITS OF DETECTION AT DIFFERENT WAVELENGTHS

% (w/v) under the conditions described, at twice the detector noise level.

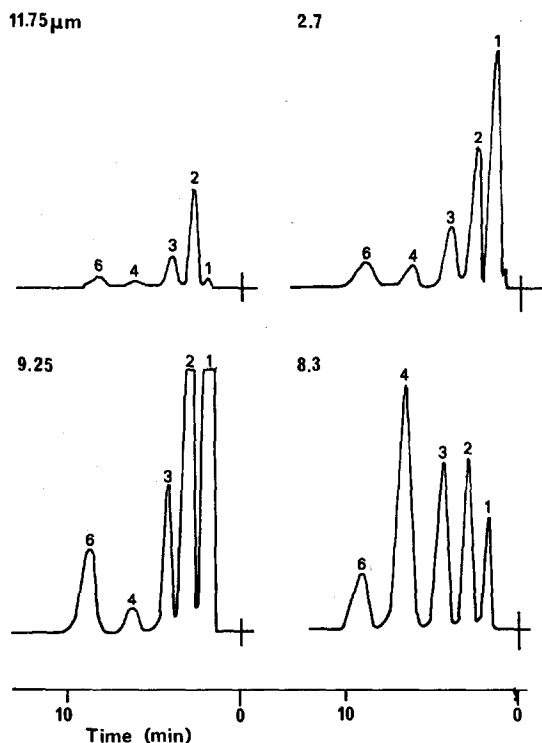| | Wavelength ($\mu$m) | | | | | |
|---|---|---|---|---|---|---|
| | 2.7 | 8.3 | 8.75 | 9.25 | 9.5 | 11.75 |
| Methanol | 0.14 | – | – | 0.03 | 0.03 | – |
| Ethanol | 0.24 | 0.16 | 0.16 | 0.03 | 0.03 | – |
| Propan-2-ol | 0.54 | 0.18 | 0.06 | 0.08 | 0.16 | 4 |
| *tert.*-Butanol | 1.4 | 0.07 | 0.10 | 0.64 | 0.64 | – |
| *sec.*-Butanol | 1.2 | 0.26 | 0.15 | 0.20 | 0.20 | 4 |
| MTBE | – | 0.10 | – | – | – | 0.6 |

Fig. 3. Infrared detector response for alcohols. Change in infrared response of alcohols with change in detection wavelength. Porapak Q, 175°C. Peak numbers as in Fig. 1.

tention time to *sec.*-butanol, there would clearly be problems if both compounds were present in a single mixture. Determination of *sec.*-butanol at 2.7 μm with subsequent correction of the apparent MTBE figure at 11.75 μm was shown to be a valid but inconvenient method when compared to normal analysis using the Porapak Q/N column.

TABLE III

ANALYSIS OF SYNTHETIC BLENDS OF OXYGENATES WITH GASOLINE

| Sample No. | Additive | Monitoring wavelength (μm) | % (w/v) added | % (w/v) found | | | | Mean | Recovery (%) |
|---|---|---|---|---|---|---|---|---|---|
| 1 | Propan-2-ol | 9.25 | 8.3 | 8.5 | 8.3 | 8.4 | 8.4 | 8.4 | 101 |
| 2 | Methanol | 9.25 | 14.7 | 14.8 | 14.8 | 14.7 | 14.8 | 14.8 | 100.7 |
|  | *sec.*-Butanol | 9.25 | 13.3 | 13.5 | 13.5 | 13.5 | 13.5 | 13.5 | 100.5 |
| 3 | MTBE | 8.3 | 0.85 | 0.88 | 0.84 | 0.86 | 0.86 | 0.86 | 101 |
| 4 | *sec.*-Butanol | 8.5 | 8.6 | 8.5 | 8.5 | 8.5 | 8.5 | 8.5 | 99 |
|  | MTBE | 8.5 | 9.1 | 9.2 | 9.3 | 9.3 | 9.3 | 9.3 | 102 |
| 5* | *sec.*-Butanol | 2.7 | 8.6 | 8.4 | 8.6 | 8.6 | 8.6 | 8.5 | 99 |
|  | MTBE | 11.75 | 9.1 | 9.3 | 9.3 | 9.3 | 9.3 | 9.3 | 102 |

    * Measured on Porapak Q with unresolved peaks and correction for cross contribution of *sec.*-butanol at 11.75 μm.

Synthetic mixtures of oxygenates with gasoline were prepared and analysed as described above. Table III shows the results obtained. Both precision and accuracy are good with experimental recoveries ranging from 101 to 102%.

Sample pretreatment was limited to dilution of the sample, where necessary, to ensure that the oxygenate peaks were within the range of linear response of the detector.

CONCLUSIONS

The use of infrared detection with a GC separation on a mixed Porapak Q/Porapak N column allows rapid identification and determination of a range of alcohols and methyl *tert.*-butyl ether in gasolines. No sample preparation is required beyond dilution with alcohol-free gasoline.

ACKNOWLEDGEMENT

REFERENCES

1 R. E. Pauls and R. W. McCoy, *J. Chromatogr. Sci.*, 19 (1981) 558.
2 J. Sevcik, *J. High Resolut. Chromatogr. Chromatogr. Commun.*, 3 (1980) 166.
3 D. Welti, *Infra-red Vapour Spectra*, Heyden and Son and Sadtler Research Laboratories Inc., London, 1970.