Determination of methyl tertiary butyl ether (MTBE) in gasoline by Raman spectroscopy

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Tribute to Daniel H. Christensen on the Occasion of his 70th Birthday

The Raman spectrum of methyl tertiary butyl ether (MTBE) was obtained and assigned as a prerequisite. Two overtone bands from CH_3 deformation and the band at ~722 cm^{-1} from the tert-butyl group were characteristic of the MTBE spectrum. Gasoline samples were also obtained in order to try to determine the MTBE content by means of these two characteristics. Most of the spectra, when excited by green laser light (514.5319 nm), had a broad background because of fluorescence. To improve the spectral results, we tried to subtract this background from the spectra. The MTBE spectrum was diluted by mixing with heptane, also having a Raman spectrum, which was studied. The ratio between the area of the band at ~722 cm^{-1} and the CH stretching bands was plotted as a function of MTBE content. A clear correlation was found, but with some uncertainty, resulting in a detection limit in the order of 30 vol. % of MTBE for the used experimental set-up. Improvements are needed before the method can be used in practice.

1 Introduction

There has been some public interest about the compound MTBE, which is sometimes used as an additive in gasoline for automobiles. The interest was caused by American investigations showing that aqueous MTBE is able to penetrate soil and thus pollute the underground drinking water reserves. In Denmark the National Environmental Agency ordered an investigation of areas around closed gasoline stations, and these investigations showed an increased MTBE concentration in the underlying water.

Determination of *wt.* % MTBE in gasoline has earlier been made by FT-Raman spectroscopy and chemometrics in the range from 0.2 to 3.262 *wt.* % O, i.e. 1.1 to 18 *wt.* % MTBE[1]. At Department of Chemistry, the Technical University of Denmark (DTU), we recently acquired a confocal micro-Raman instrument and we investigated the possibility of using this instrument as a means of analyzing the MTBE content in various gasoline samples.

It was thought to be of interest to investigate if it is possible to determine how much the MTBE content actually varied between different gasoline types sold in Denmark, and if the MTBE content varied for the same type through the year 1998.

MTBE

MTBE is an acronym for <u>m</u>ethyl <u>t</u>ertiary <u>b</u>utyl <u>e</u>ther ($C_5H_{12}O$), C.A. reg. no. 1634-04-4: 2-methoxy-2-methylpropan. The structural formula for the compound is shown in Fig. 1. It is a colorless, flammable liquid, which has both polar and non-polar properties, i.e. it can be dissolved in both water and gasoline. MTBE is an example of an oxygenate, i.e. a compound containing oxygen. Oxygenates often exhibit the effect to increase the gasoline octane number. Thus, if MTBE is added gasoline, the combustion conditions in a motor are improved, because a higher compression can be achieved without self-ignition. The result is a smaller emission of polluting substances (e.g. CO) for the same motor efficiency. There is a lot of different oxygenates which can be used for this purpose, e.g. tetraethyl lead, methanol or ethanol, but frequently MTBE is used today, because it among other things does not contain lead, it is cheap to produce, easy to mix with gasoline and because it dilutes aromatic components like toxic benzene[2,3].

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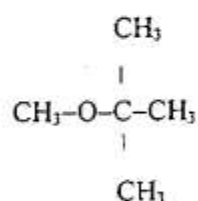CH_3 \\
| \\
CH_3-O-C-CH_3 \\
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CH_3
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Fig: 1. The structural formula of MTBE.

The geometry of the MTBE molecule has not been determined due to the internal rotation, but attempts have been made. It has been shown that ETBE (<u>e</u>thyl <u>t</u>ertiary <u>b</u>utyl <u>e</u>ther) has C_S symmetry, but since the MTBE molecule has two atoms with small b-principal axis coordinates, it is more difficult to determine this structure than that of ETBE[4]. The highest possible symmetry MTBE can adopt is C_S. With 18 atoms it has $(3 \cdot 18)-6 = 48$ modes of vibration, of which 27 belong to A' (total symmetric vibrations) and 21 to A''. A complete analysis of the vibrations has not been made.

2 Experimental

Instrumentation

The Raman spectra were obtained by use of a confocal micro-Raman spectrometer (DILOR-XY). An Ar-ion laser ($\lambda_{air} = 514.5319$ nm, ~200 mW) was used for excitation and the

scattered radiation was detected by a CCD detector with 1024 x 256 pixels cooled by liquid nitrogen. All spectra were obtained by use of the second monochromator (with a grating of 600 grooves/mm) in the direct pass mode. The Rayleigh filtration was done, not by the foremonochromator, but by a super plus holographic notch filter from Kaiser Optics. Samples were placed directly under the microscope (10 x objective), i.e. by use of a 180° collection geometry.

The IR spectrum was acquired with a Fourier transform infrared spectrometer (Perkin Elmer FT-IR 1760X) in the region 4000-400 cm^{-1}. The spectrum consisted of 4 scans at 4 cm^{-1} resolution. For the measurement, a 0.0125 mm liquid cell with KBr windows was used.

Obtained Raman and IR band wavenumbers are given in Table 1.

Chemicals

We had the following chemicals at hand: Heptane (>99.5% by vol., Fischer), MTBE (>99.5% by vol., Fluka) and MTBE (>99.5% by vol., Merck). All chemicals were used without further purification. Several MTBE/heptane mixtures were made volumetrically and stored in 0.2 ml injection glasses sealed with an Ai-stopper. Several unleaded gasoline samples, all with the octane number 98, were collected from different gasoline stations in the Copenhagen area during a period of 3 months in the summer of 1998.

3 Results and Discussion

The Raman Spectrum of MTBE
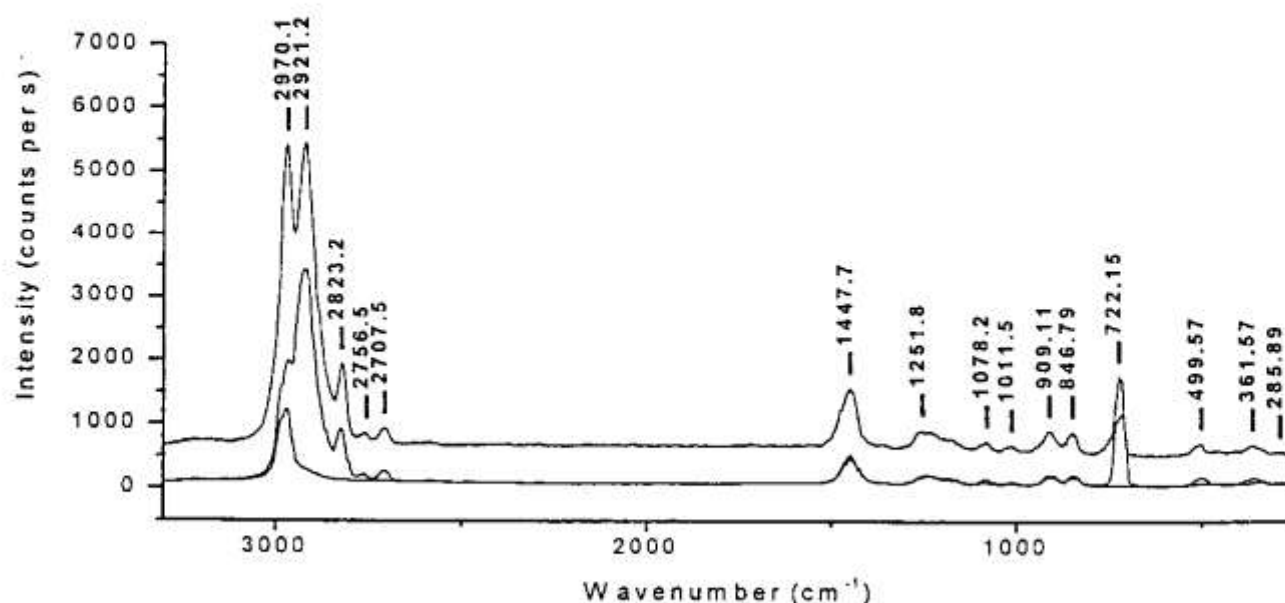
The Raman spectrum of MTBE is shown in Fig. 2.

Fig: 2. Raman spectrum of MTBE. Upper curve: no polarizer. The lower curves show VV and VH polarization, respectively.

In addition to the Raman spectrum obtained with no polarizer we also obtained Raman spectra of MTBE with VV and VH polarization. In Fig. 2 it is seen that some of the bands are polarized ($I_{VH} / I_{VV} < 0.75$) and some are depolarized ($I_{VH} / I_{VV} = 0.75$). From this observation it is deduced that MTBE probably has C_S symmetry The band positions and polarization behavior are given in Table 1.

The most intense bands in the spectrum occur in the CH stretching region of 3000-2800 cm^{-1}. The bands at 2970 cm^{-1} and 2921 cm^{-1} are the asymmetric and symmetric stretchings, respectively. Furthermore, there is a characteristic band at a lower wavenumber (2823 cm^{-1}). The assignment of this band is obtained by noting that CH_3COOCH_3 in earlier studies on its IR spectrum has shown a band at 2845 cm^{-1}, and by deuteration (i.e. measurements on CD_3COOCH_3) it has been shown that this band must be due to the O-CH$_3$ group[5-7]. FT-IR and Raman spectra in the literature[8,9] show that O-CH$_3$ groups normally have their infrared active CH stretching bands at 3000-2800 cm^{-1}, 2970-2920 cm^{-1} and 2850-2820 cm^{-1}. Thus, it is obvious to conclude that the characteristic band at 2823 cm^{-1} in the Raman spectrum of MTBE is due to CH stretching in the methyl radical connected to oxygen.

CH$_3$ bending vibrations are seen as bands near ~1448 cm^{-1} (asymmetric deformation), but these bands are not well resolved. For molecules with methyl groups, a symmetric CH$_3$ umbrella deformation at ~1375 cm^{-1} is normally not seen in Raman spectra, only in IR spectra. On the other hand, the overtone (2v) of that vibration is seen in the Raman spectra but not in the IR spectra (IR and Raman spectroscopy are often complementary techniques).

In tert-butyl compounds the symmetric CH$_3$ umbrella deformation splits up in two bands (~1368-1366 cm^{-1} and ~1381-1391 cm^{-1}) of different intensity[10]. The band with the lowest wavenumber is the most intense in IR. This splitting is indicated by arrows in the FT-IR spectrum of MTBE (Fig. 3). The obtained spectrum is in agreement with previous recordings[11]. In the Raman spectrum (Fig. 2) the splitting is seen also for the two overtones (2708 cm^{-1} and 2757 cm^{-1}). Also here, as in IR, it is observed that the one with the lowest wavenumber has the strongest intensity.
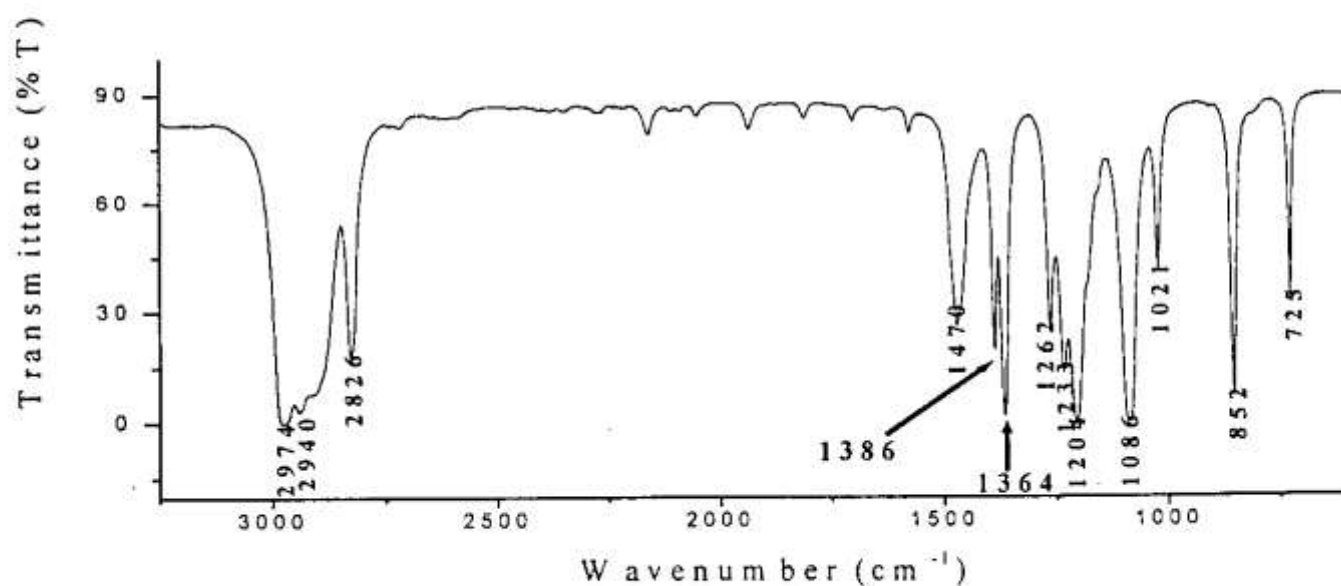

Fig: 3. The FT-IR spectrum of MTBE.

Another characteristic feature in the Raman spectrum of MTBE is the band at ~722 cm^{-1}, which is without doubt due to the symmetric C-C stretching involving the tertiary carbon in the tert-butyl group[3,12,13].

Against this background we reach the preliminary conclusion: If a gasoline sample contains MTBE, the Raman spectrum should be expected to show characteristic overtone bands at 2708 and 2757 cm^{-1} and a fundamental band at ~722 cm^{-1}. The latter is also mentioned in the previous literature[3].

In Denmark MTBE is added to gasoline, according to information given by gasoline companies, in amounts up to ~5% by vol. The additions have until now only been made for octane 98 gasoline. With such a low concentration it was not expected to see the two overtones in the Raman spectrum (even in the spectra of pure MTBE these bands are weak). By use of the band at 722 cm^{-1}, on the other hand, we have a possibility to detect MTBE in gasoline samples at a 5% level.

Table 1. Characteristic Raman and IR bands of MTBE.

Wavenumber (cm^{-1}) Raman (liquid)	Wavenumber (cm^{-1}) IR (liquid)	Tentative assignments based on refs. 5-10, 12-14
2970 (s) dp?	2974 (s)	v_e (CH$_3$) / A"
	2940 (s)	v_e (CH$_3$) (t-butyl group)
2921 (s) p		v_s (CH$_3$) / A'
2823 (m) p	2826 (s)	v (CH$_3$) (methoxy group) / A'
2757, 2707 (w) p		overtones from symmetric CH$_3$ umbrella deformation δ_s / A'
	1470 (m-s)	δ_e (CH$_3$) (t-butyl group)
1448 (m) dp		δ_e (CH$_3$) (methyl group) / A"
	1386, 1364 (s)	δ_s (CH$_3$) (umbrella deformation) / ?
1252 (w) dp	1262 (m-s)	? / A"
	1233 (s)	δ_s (CH$_3$) (methyl group)
	1204 (s)	v_e (CC) (t-butyl)
1078 (w) p	1086 (s)	v (CO) / A'
1012 (w) p	1021 (m)	v (CC)
910 (w) dp		ρ (CH$_3$) / A"
847 (w) dp	852 (s)	? / A"
722 (m) p	725 (m-s)	v_{sym} –C(CH$_3$)$_3$ / A' (symmetric skeletal vibration of the t-butyl group).
500 (w) p		? / A'
362 (w) p		τ (CH$_3$) (twisting) / (A')

s = strong, m-s = medium to strong, m = medium, w = weak. v_s, v_e etc. are defined in e.g. ref. 9. p = polarized, dp = depolarized.

Raman Spectra of Gasoline

All collected gasoline samples showed a strong fluorescence. Thus, most of the Raman spectra were measured on a broad background of this fluorescence. Examples of spectra of a gasoline sample are shown in Fig. 4a. The CH_2 and CH_3 bendings are faintly seen around 1440 cm^{-1} and the region of CH stretching gives clear information: Aliphatic CH stretchings are observed at ~2900 cm^{-1} and aromatic CH stretchings at ~3040 cm^{-1} (our goal is subsequently to investigate whether our Raman instrument can be used to determine the aromatic content in gasoline). Thus, the Danish gasoline collected clearly had a non-vanishing content of aromatic hydrocarbons. Two MTBE overtone bands around 2750 cm^{-1} could not, as expected, be observed in the spectrum, and neither the band at 722 cm^{-1}. Whether this is because of fluorescence obscuring the bands or due to low MTBE concentrations cannot be concluded.
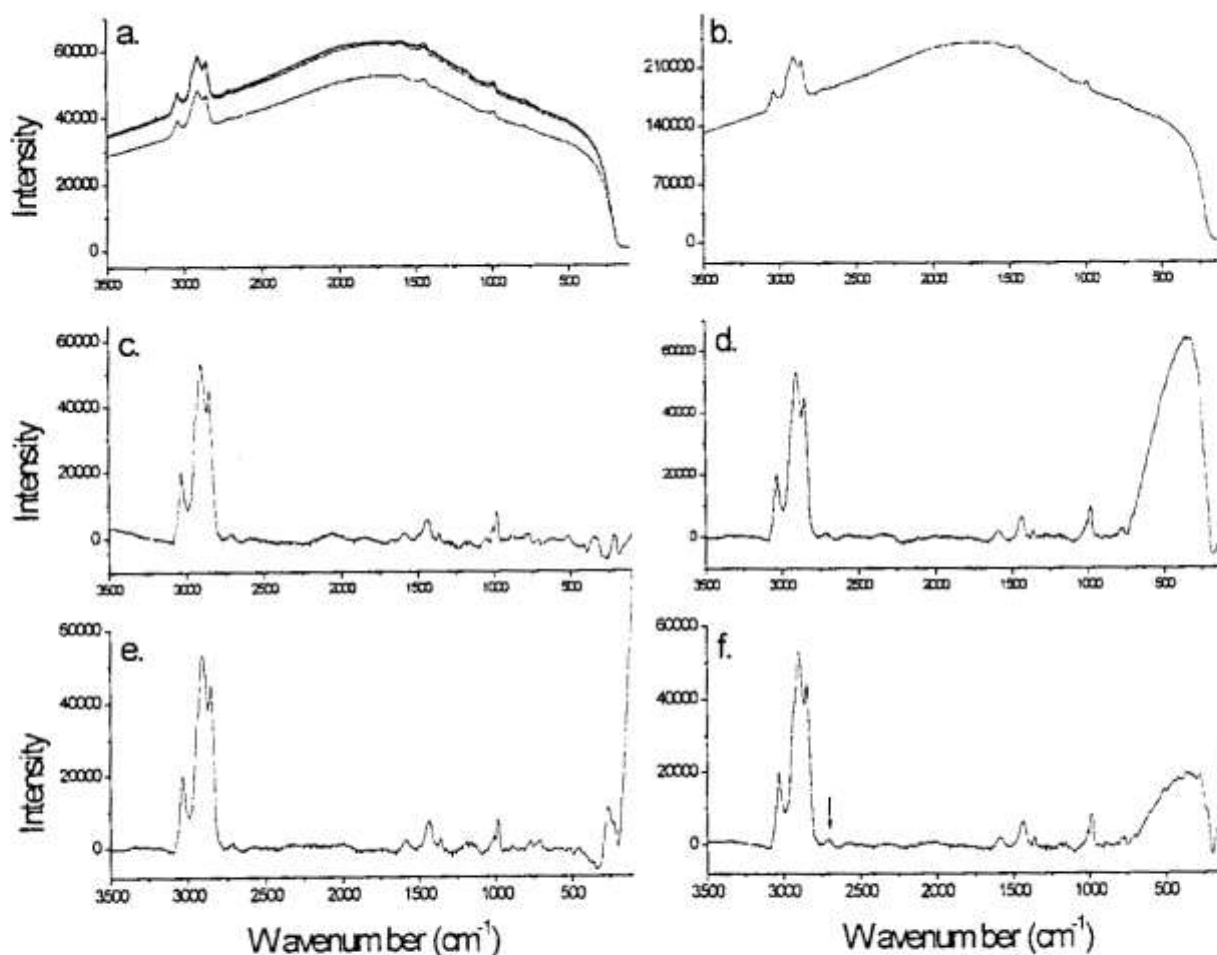

Fig: 4. Raman spectra of an octane 98 gasoline sample. a) The originally obtained spectra and b-f) mathematical treatment of the spectra from a.

We tried to correct for the background in the spectra of Fig. 4a, and the results are shown in the rest of Fig. 4. The spectra of the gasoline sample shown in Fig. 4a are three spectra

obtained successively, each in 10 seconds, and one spectrum obtained after 15 min. of excitation (lowest fluorescence intensity). These four spectra show i) reproducibility and ii) a decreasing fluorescence background caused by the influence of the laser light. The latter observation that it is possible to "burn away" some fluorescence is well-known and widely described in the literature. We then tried to treat the spectra mathematically by means of software (Speclab v 2.01) associated with our Raman instrument. First we added up the spectra. This is shown in Fig. 4b, which is the sum of the four spectra from Fig. 4a. Then we made a baseline correction by introducing a suitable and adjustable polynomial and subsequently subtracted it from the spectrum. Figs. 4c-e are the results of such modifications in dependence on the polynomials used. First order (4c), second order (4d) and third order (4e). Fig. 4f is the average of the spectra in Figs. 4c-e.

The last corrected spectrum (Fig. 4f) looks remarkably better than the spectra in Fig. 4a. The bands are clearer, e.g. the overtone from CH_3 symmetric deformation ~2712 cm^{-1} can be seen. Although the spectrum is somewhat better, the method has intrinsic weaknesses. It is difficult to be sure that all the bands are "real bands". On the other hand, repeated measurements typically gave reproducible results. More advanced mathematical methods exist which could perhaps be used.

After these somewhat negative results we tried instead to investigate, in an artificial gasoline mixture made by ourselves, how large the MTBE content should be to be visible in the Raman spectrum. By using known concentrations of heptane and MTBE, we then determined experimentally to what content MTBE could be detected by Raman spectroscopy. Heptane was chosen instead of gasoline because heptane gave lesser fluorescence than gasoline. In this way we wanted to see if the method was usable at all.

Raman Spectra of MTBE in Heptane

We obtained Raman spectra of heptane solutions containing 30, 40, 50, 60, 75, 80, 90 and 100 vol.% of MTBE. These spectra are shown in Fig. 5. As it is seen, all the spectra show fluorescence except the spectrum of pure MTBE and the spectrum of pure heptane (not shown). The fluorescence arises from the liquids themselves when mixed. The two overtone bands at ~2708 cm^{-1} and ~2757 cm^{-1} are faintly seen in the spectra of 75-100 vol.% of MTBE, but were not seen in lower concentrations. The intensity of the band at 2823 cm^{-1} (CH stretching in the $O-CH_3$ group) clearly decreases as the solution weakens with respect to MTBE content. The characteristic band at ~722 cm^{-1} was observed in all the spectra, but only weakly in the spectrum of the 30 vol.% MTBE solution. Without doubt it is because of the fluorescence. It is seen that the more dilute the solution became, the weaker the band at ~722 cm^{-1} was in comparison to the CH stretching bands.
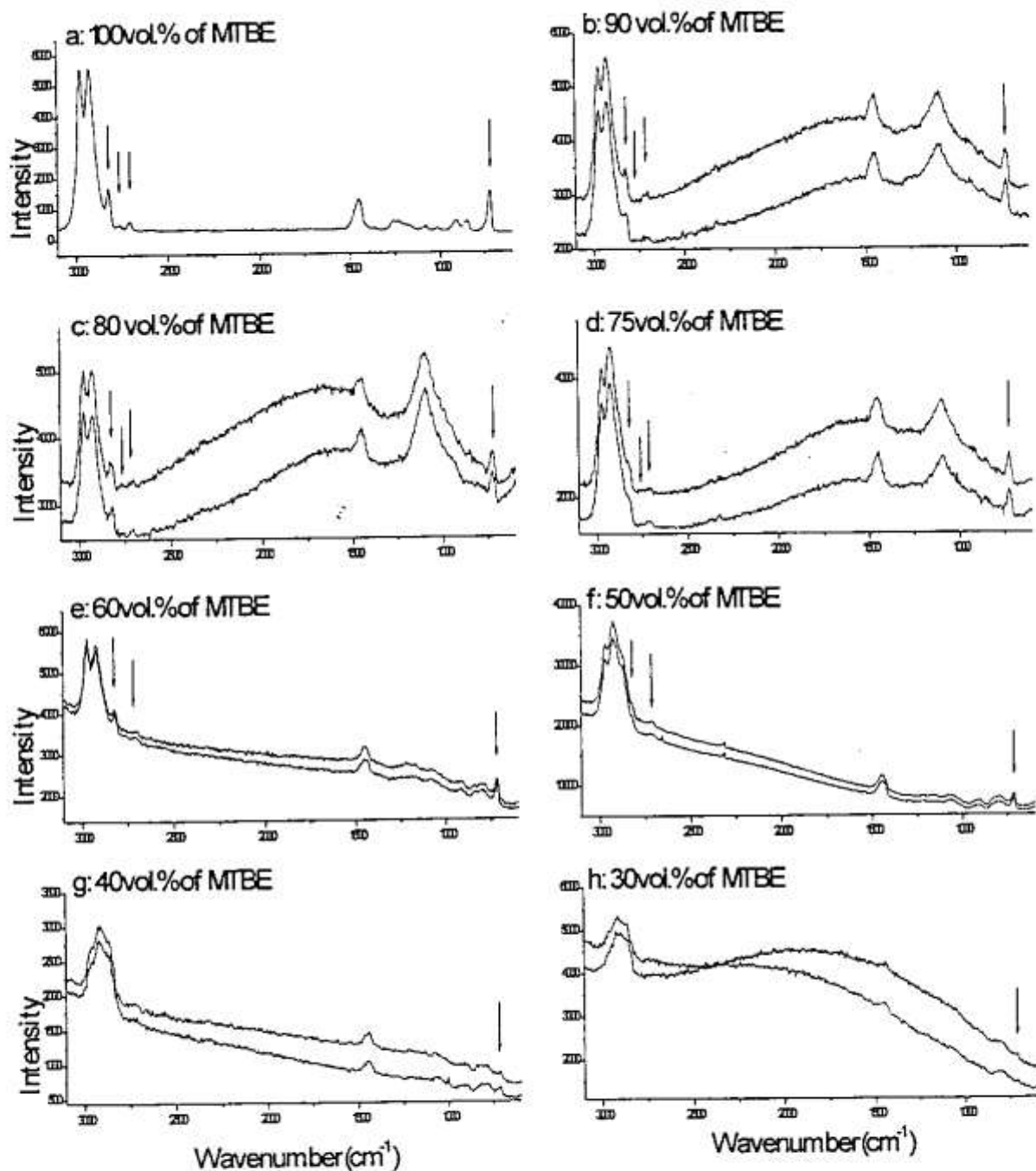
Fig: 5. The Raman spectra of heptane / MTBE solutions.

The band at ~722 cm^{-1} must be due to the MTBE, whereas the CH stretching bands (3000-2900 cm^{-1}) can arise from vibrations in both MTBE and heptane. Theoretically, there should be a correlation between the area ratios of these bands and the vol.% of MTBE. If such a correlation can be found it should be possible to determine the volumetric MTBE percentage in an unknown binary sample, simply by obtaining its Raman spectrum. We then tried to do this. The result is shown in Fig. 6. The area ratio is the area under the band at ~722 cm^{-1}

divided by the area under the CH stretching bands. The areas were found by using the software associated with the Raman instrument, leaving out the fluorescence background by user-guided experimentation. A clear tendency was observed. The points have some uncertainty, but by linear regression forced through the origin a quite reasonable fit was obtained ($R^2 = 0.944$).
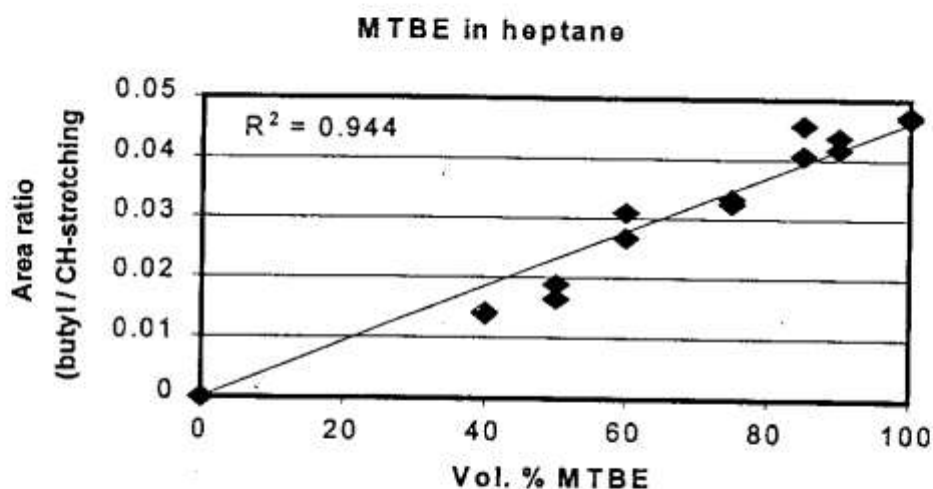
MTBE in heptane

Fig: 6. Plot of area ratio, $A(\sim722 \text{ cm}^{-1}) / A(3000\text{-}2800 \text{ cm}^{-1})$, as a function of the vol. % MTBE.

4 Conclusion

Our measurements on pure MTBE showed a Raman spectrum with finely resolved bands and no fluorescence. Two overtone bands from the symmetric CH_3 deformation at 2708 cm^{-1} and 2757 cm^{-1} (weak intensity) were characteristic for the Raman spectra of MTBE in regard to other corresponding compounds to which it could be compared (e.g. ethanol and methanol). The band at ~722 cm^{-1}, coming from the tert-butyl group, was so intense that it ought to be seen, even at low MTBE concentrations. Our aim was to investigate whether Raman spectroscopy using green Argon 514.5 nm excitation could be used to determine the MTBE content in gasoline. Because of strong fluorescence we must conclude that the detection limit (at the moment) is around 30 vol.% in MTBE / heptane solutions. The band at ~722 cm^{-1} has not at all been observed in any of the measured gasoline samples.

Our Raman spectroscopic measurements of heptane samples with addition of known amounts of MTBE were influenced by a broad fluorescence background, though not as much as for the gasoline samples. The band at ~722 cm^{-1} was observed when the MTBE content was more than 30 vol.%. At lower concentrations it was not observed, presumably because of fluorescence. The method was used without correction for the fluorescence background. We plotted the ratio between the area of the band at ~722 cm^{-1} and all the CH stretching bands as a function of MTBE content. A clear correlation ($R^2 = 0.944$) was found, but the uncertainty seems to be too large for the area method to be used to define the MTBE content (at least

without improvements).

In our Raman spectra aromatic CH stretching was observed for all gasoline samples. This seems to show that our Raman instrument might be of use in determining the aromatic content in gasoline. We also plan to employ different measures in order to avoid the fluorescence problem. Such a measure would be to use another wavelength, but so far we have not had satisfactory results.

Acknowledgements

References

1. Cooper J B, Wise K L, Welch W T, Bledsoe R R, Summer M B, *Appl. spectrosc.*, 50 (1996) 917.
2. Iversen E, *Ingeniøren (Copenhagen)*, 11 (1998) 4.
3. www.arb.ca.gov/cbg/pub/mtbebp.pdf.
4. Suenram R D, Lovas F J, Pereyra W, Fraser G T, Walker, A R H, *J. Mol. Spectrosc.*, 181, (1997) 67.
5. Nolin B, Jones R N, *Can. J. Chem.*, 34 (1956) 1382.
6. Henbest H B, Meakins G B, Nicholls B, Wagland A A, *J. Chem. Soc.*, (1957) 1462.
7. Dalton F, Hill R D, Meakins G D, *J. Chem. Soc.*, (1960) 2927.
8. Pouchert C J, *The Aldrich library of FT-IR spectra*, (1985).
9. Lin-Vien D et al., *The Handbook of infrared and Raman Characteristic Frequencies of Organic Molecules*, (Academic Press, Boston) 1991.
10. Meloan C E, *Elementary Infrared Spectroscopy*, (Mcmillan, New York) 1963.
11. Bruker, *Merck FT-IR Atlas*, (VCH Verlagsgesellschaft mbH, Weinheim) 1988
12. Horace A O, *Anal. Chem.*, 32 (4) (1960) 509.
13. Dean J A, *Handbook of Organic Chemistry*, (McGraw-Hill, New York) 1987.
14. Egava T, Moriyama H, Takeuchi H, Konaka S, Siam K, Schäfer L, *J. Mol. Struct.*, 298 (1993) 37.