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Detection of Methyl *tert*-butyl Ether (MTBE) in Gasoline Fuel using FTIR: ATR spectroscopy

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Abstract

Methyl tertiary-butyl ether (MTBE) is the primary oxygenate additive used in gasoline fuel in compliance with the Clean Air Act requirements to reduce emission level of spark ignited automotive engines. However, MTBE is also classified as a possible carcinogen and there have been several cases where the compound is found to contaminate soil and ground water through its used as oxygenate in fuel. Therefore in the present work gasoline samples collected from different filling stations in Aizawl were analyzed for the presence of MTBE using Fourier Transform Infrared – Attenuated Total Reflectance (FTIR-ATR) spectroscopy in the mid IR region. Out of 14 samples tested one sample is found to contain MTBE. The presence of the oxygenate in gasoline is identified from its distinct IR absorption bands at 1203, 1085 and 852 cm^{-1} due to the CC and CO vibrational modes of the molecule. IR mode assignment of gasoline fuel in the 650-3750 cm^{-1} region is also discussed and presented.

Keywords: Gasoline, FTIR, oxygenate, MTBE.

Introduction

Transportation powered by combustion of fossil fuels in internal combustion engines is one of the major sources for air pollution[1]. The pollutants emitted from automotive engines exhausts are mainly nitrogen oxides (NOx), carbon monoxide (CO), unburned hydrocarbons (UBHC), particulate matters (PM) and volatile organic compounds (VOC)[2]. These pollutants are harmful to human health as they can cause acute and chronic disease symptoms upon inhalation or ingestion[3,4]. Out of the different vehicular pollutants, most of them except NOx are formed due to incomplete combustion of the hydrocarbon fuels. Therefore to improve hydrocarbon combustion in automotive engines and hence to reduce the emission levels of CO, UBHC and other pollutant matters, the Clean Air Act (CAA) Amendments came out in 1990 which layout new regulation for the composition of fuels especially gasoline[5]. According to this act, the refining industry and their petrochemical laboratories are required to add oxygenates to gasoline in order to meet attainment levels of carbon monoxide and unburned hydrocarbons[3]. Oxygenates are chemical compounds containing one or more oxygen atoms in their chemical structure. The oxygen atom in oxygenate help in more complete combustion gasoline fuel thus reducing the emission of CO and other pollutants. Among different oxygenates which can be used for this purpose, MTBE (methyl *tertiary*-butyl ether) has been the most widely used fuel blending component because of its low production cost, high solubility in gasoline as well as easy transportation and storage[6]. However, there has been controversy over the use of MTBE as an oxygenate for making cleaner burning gasoline[7,8]. MTBE has been classified as a possible human carcinogen and there are many reports on groundwater contamination by the additive through release from leaking gasoline storage tanks[9]. As a result, the chemical has been banned from being used in gasoline in many parts of US, and other additives, primarily ethanol, are used as the oxygenate[10]. However, in India and many other Asian countries MTBE still continue to be the primary oxygenate in gasoline. Therefore a reliable method is needed for constant monitoring of presence of the oxygenate in gasoline to check and avoid its possible ground water contamination in regions where the compound is still in used as oxygenate. Accordingly the present work is undertaken to analyze the quality of gasoline fuel in Aizawl for the presence of MTBE using FTIR-ATR spectroscopy.

Material and Methods

A batch of gasoline samples for analysis was collected in the month April to May, 2015 from 14 different filling stations within Aizawl city. Out of these 14 samples, 12 are MS Quality and the other two are of Premium Quality. The IR absorption spectra of the samples are recorded directly without further purification using ABB-Bomem FTIR spectrometer with ZnSe ATR crystal (Pike Technologies). Data acquisition and spectral processing were done with Horizon MB 3000 software. Each IR spectrum is the average 20 number of scans at 4 cm^{-1}resolution.

Results and Discussion

Conventional gasoline also called petrol in India is a mixture of more than 200 different hydrocarbons containing 4 to 12 carbon atoms per each molecule. The actual composition of gasoline varies widely, depending on the crude oils used, the refinery processes available, the overall balance of product demand, and the product specifications. The typical composition of gasoline hydrocarbons (% volume) consists of 4–8 % alkanes; 2–5 % alkenes; 25–40 % isoalkanes; 3–7 % cycloalkanes; l–4 % cycloalkenes; and 20–50 % total aromatics[11]. Apart from these primary hydrocarbons, a number of additives and blending agents are added to the hydrocarbon mixture to improve the performance and stability of gasoline.

Figure-1 shows the FTIR-ATR absorption spectrum of gasoline in the 600–3750 cm^{-1} region. The spectrum is characterized by a broad absorption band around 3293 cm^{-1} followed by CH stretch of aromatics compounds at 3030 cm^{-1}. Group of strong bands in the 3000-2750 cm^{-1} region are due to CH stretching vibrations of alkanes. The broad absorption band at 3293 cm^{-1} is characteristic of stretching vibrational of OH functional group coming from either water or alcohol. IR absorption peaks observed in the 1300-1700 cm^{-1} region are primarily due to C=C and CH (scissoring) of the skeletal modes. Peaks below 1000 cm^{-1} are mostly due to out-of-plane vibrations aromatic and other cyclic hydrocarbons. Tentative mode assignment of the prominent IR peaks is given in table-1**.**

Other gasoline samples including the premium grades also shows spectral features similar to figure-1. However, careful examination of the spectra in the 800-1250 cm^{-1} region reveals that out of the 14 samples tested one sample is found to exhibit distinct features as shown in figure-2. Three absorption peaks of modest intensity are observed at 1203, 1085, and 852 cm^{-1} in the IR spectrum of this sample. These peak positions are found to be in good agreement with the characteristic vibrational modes of MTBE. The molecular structure of MTBE is shown in figure-3. In MTBE the CH_3-C stretch of the t-butyl group and C-O-C asymmetric stretch of the molecule are reported at 1204 and 1085 cm^{-1} respectively[12]. The presence of two (or more) strong bands in this region is an indication that there is branching on the ether carbons. Moreover, the C-O-C symmetric stretch in MTBE was reported at 851 cm^{-1}. Therefore, we can say with confidence that the IR bands at 1203, 1085 and 852 cm^{-1} observed in one of the gasoline sample is due to presence of MTBE oxygenate.

Table-1
Tentative IR mode assignment of gasoline fuel

Vibrational mode	Frequency(cm^{-1})
ν_sOH (alcohol/water)	3293
νCH *(aromatic)*	3030
$\nu_{as}CH_3$	2959
ν_sCH_2	2927
ν_sCH_3	2874
νC=C	1650
δCH	1460
δ_sCH_3	1376
νC-C	1031
δCH(aromatic)	800-650

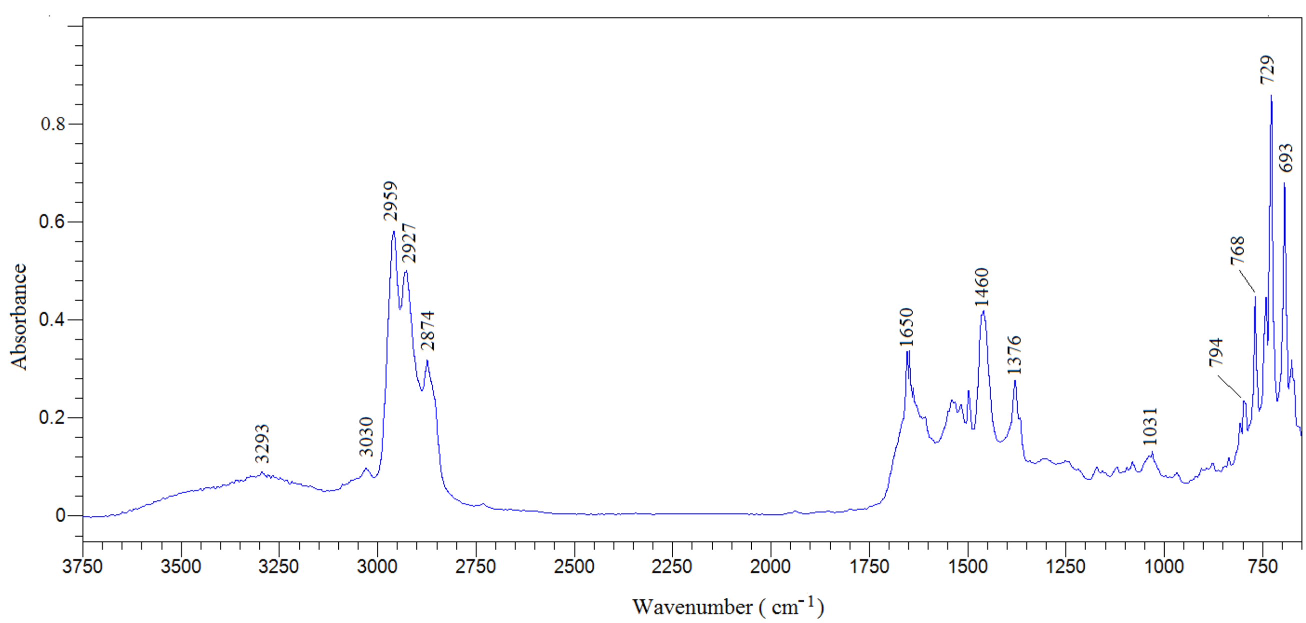

Figure-1
FTIR-ATR spectrum of gasoline (MS quality) in the 650-3750 cm^{-1} region

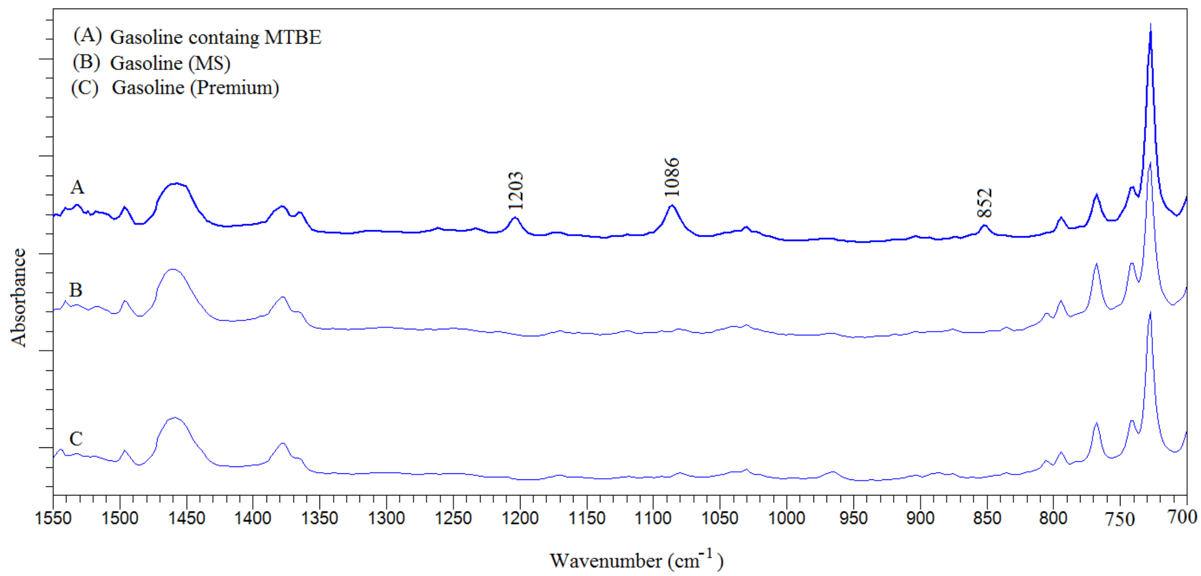

Figure-2
Comparison of three different quality of gasoline samples in the 700-1550 cm^{-1} region: (A) Gasoline containing MTBE (B) Gasoline MS quality (C) Gasoline Premium quality

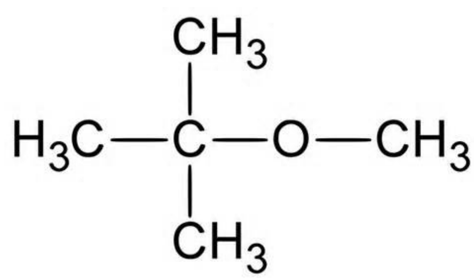

Figure-3
Molecular structure of MTBE

Conclusion

Gasoline samples collected from different filling stations within Aizawl city are analyzed for the presence of MTBE oxygenate using FTIR-ATR technique in the mid IR region. From a total of 14 samples tested including premium quality, one sample is found to contain MTBE. The presence of the oxygenate in gasoline can be easily identified from its distinct IR absorption bands at 1203, 1085 and 852 cm^{-1} due to the CC and CO vibrational modes of the molecule.

Acknowledgement

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