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Analysis of petrol quality of Aizawl for oxygenate additives by FTIR-ATR spectroscopic technique

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Abstract

Clean air and green world are the requirements of today. Transportation powered by conventional fossil fuels is the largest single source of air pollution. To improve the air quality by reducing of vehicle exhaust emission levels, oxygenates has been added to petrol since 1990 as per Clean Air Act Amendments. The present report is an analysis of petrol for the presence of oxygenates using FTIR-ATR technique in the mid-IR region. Petrol samples for analysis were collected from different filling stations within Aizawl city. Out of 9 samples tested including extra-premium (XP) grade, only one sample is found to contain oxygenate, namely, methyl *tertiary*-butyl ether (MTBE). The presence of the oxygenate in petrol can be identified from its distinct IR absorption bands at 1203, 1085 and 852 cm^{-1} due to the C-C and C-O vibrational modes of the molecule. IR mode assignment of the fuel in the 650-3750 cm^{-1} is also discussed and presented.

Key words: Aizawl; Petrol quality; FTIR; oxygenate; MTBE.

Introduction

In India, ambient air pollution is one of the major factors of hazards to human health.[1] Transportation powered by conventional fossil fuels is the largest single source of air pollution.[2] The automotive exhausts containscarbon monoxide (CO), unburnt hydrocarbons (UBHC), oxides of nitrogen (NOx), and particulate matters. Inhalation of CO and UBHC can cause many human health disorders, like dizziness, respiratory problems, mental retardation, etc.[3-5] Such pollutants are also found to cause detrimental effects on animal and plant life, in addition to environmental disorder.[6]

One of the crucial parameters that influence the formation of pollutant gasses in internal combustion engines is the nature of the fuel and its additives. Catalytic converter in the exhaust pipe can reduce majority of the emissions but not to sufficient levels. To improve the air quality by reducing of vehicle exhaust emission levels the Clean Air Act Amendments came out in 1990 which providesnew regulation for the com-

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position of fuels and particularly petrol.[7] According to this act, the refining industry and their petrochemical laboratories are required to add oxygenates to petrol in order to meet attainment levels of carbon monoxide and unburned hydrocarbons.[8] Oxygenates are chemical compound containing oxygen as a part of their chemical structure; the most widely used oxygenates being methyl *tertiary*-butyl ether (MTBE) and ethanol. With the introduction of oxygenate, a reduction of ambient CO by about 10% is envisaged.[9] Presence of oxygenates in petrol helps in a more complete combustion of the hydrocarbon fuel in the engines resulting in lower emission of CO, UBHC, soot, improved engine performance and better fuel economy. Therefore, understanding the quality of fuel that we use every day for transportation with respect to oxygenates is an important step in air quality control.

Several studies have proven that IR spectroscopy, especially, FTIR is a versatile, efficient and accurate analytical technique for the determination of fuel additives and the estimation of key petrol properties.[10,11] It enables the selective recognition of different species in relation to their specific molecular vibrations resulting in distinctive absorption bands in the corresponding spectral region. In contrast to NIR (near infrared) methods, MIR (mid infrared) spectroscopy provides access to the comparatively strong fundamental modes of organic molecules, and individual fuel components can be differentiated by their characteristic pattern of absorption bands. Therefore, in the present work petrol samples collected from different filling station within Aizawl city were analysed for the presence of oxygenates using MIR FTIR-ATR spectroscopic technique.

Materials and Method

Petrol samples for analysis were collected during April to May, 2015 from different filling stations within Aizawl city, including MIZOFED (Treasury Square), Fire Department (Hunthar), Biakliana (Ramhlun South), Zangena (Ramhlun North). Lalboih (Hunthar), Singson (Hunthar), and Ruatkima (Sairang Road). There are a total of 9 samples, out of which 7 are regular quality and the other two are extra-premium (XP). The XP samples were obtained from MIZOFED and Zangena pump stations. The IR absorption spectra of the samples were 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 15 number of scans at 4 cm^{-1} resolution.

Results and Discussion

Conventional petrol is mostly a blended mixture of more than 200 different hydrocarbon liquids ranging from those containing 4 to 12 carbon atoms per each molecule. The composition of petrol varies widely, depending on the crude oils used, the refinery processes available, the overall balance of product demand, and the product specifications. The typical petrol hydrocarbons (% volume) consists of 4-8 % alkanes; 2-5 % alkenes; 25-40 % isoalkanes; 3-7 % cycloalkanes; 1-4 % cycloalkenes; and 20-50 % total aromatics.[12] 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 petrol.

Figure 1 shows the FTIR-ATR absorption spectrum of petrol sample obtained from MIZOFED in the 600-3750 cm^{-1} region. The spectrum is characterized by a broad absorption 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 alkyl stretching vibrations of alkanes. The broad absorption at 3293 cm^{-1} is characteristic of stretching vibrational mode 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

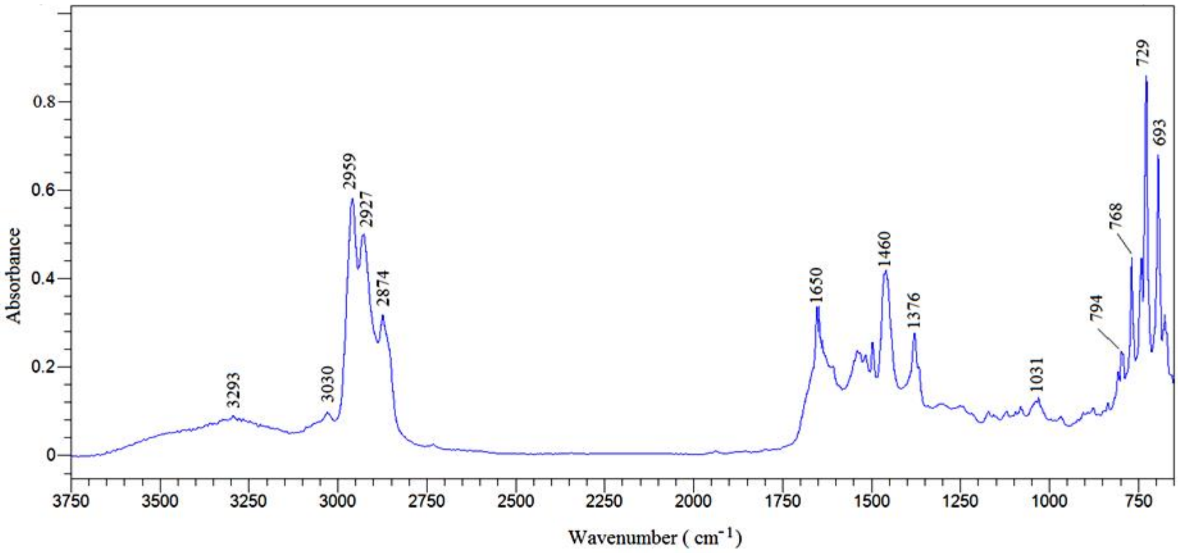

Figure 1. FTIR spectrum of petrol sample from MIZOFED (regular) in the 650-3750 cm^{-1} region.

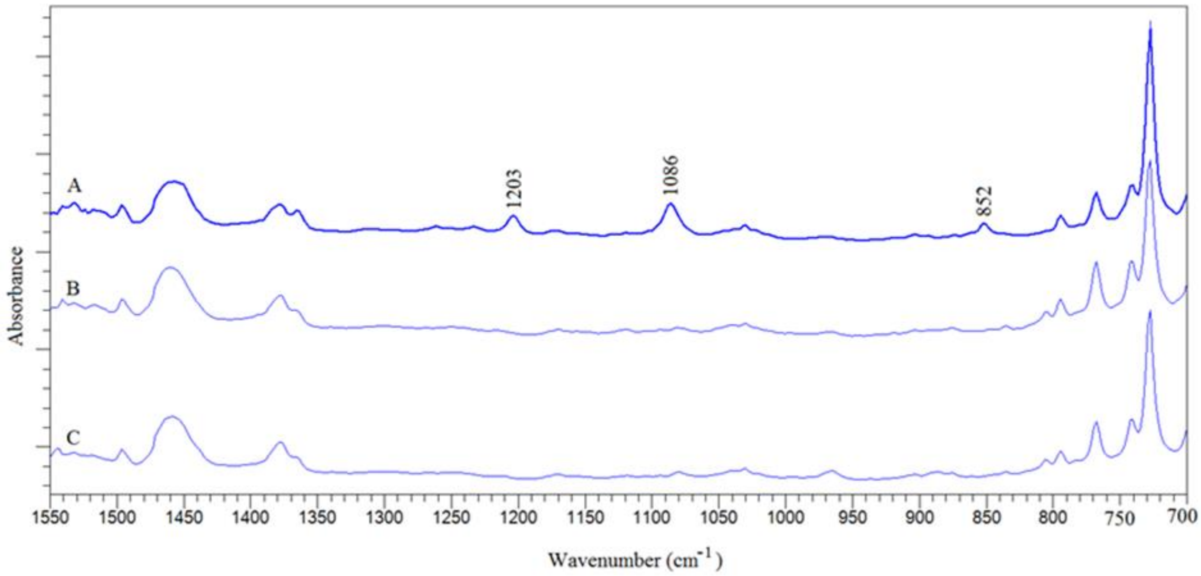

Figure 2. Comparison of FTIR spectra of three different petrol samples in the 700-1550 cm^{-1} region: (A) Ruatkima (regular) (B) MIZOFED (regular) (C) Zangena (extra-premium).

assignment of the prominent IR peaks is given in Table 1.

Other samples including the premium grades also exhibit spectral features similar to Figure 1 and therefore they are not shown separately. However, careful examination of the spectra in the 800-1250 cm^{-1} region reveals that out of the 9 samples tested the sample from Ruatkima filling station is found to exhibit distinct features in comparison to other regular as well as XP grades 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. Out of these bands, the 1085 and 852 cm^{-1} are char-

Table 1. IR mode assignment of petrol.

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

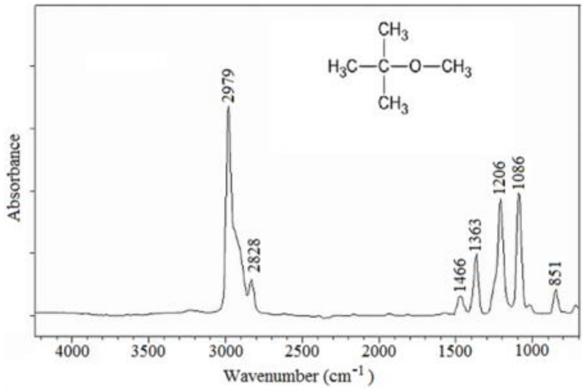

Figure 3. FTIR spectra of MTBE and its molecular structure.

acteristics of C-O stretching modes. In petrol the CO modes can come from either ether or ethanol as they are the most widely used oxygenates, and the observed CO modes are found to be more closely related with ether, especially MTBE than ethanol. The molecular structure and IR spectrum of MTBE are shown in Figure 3. Strong peaks at 1206 and 1086 cm^{-1} are due to the CH_3-C stretch of the t-butyl group and C-O-C asymmetric stretch of the molecule, respectively.[13] The presence of two (or more) strong bands in this region is an indication that there is branching on the ether carbons. Moreover, IR absorption band due to C-O-C symmetric stretch is also observed at 851 cm^{-1}. Thus we can see by comparison of Figure 2 & 3 that IR bands at 1203, 1085 and 852 cm^{-1} are in good agreement with the C-O and C-C modes of MTBE with respect to peak positions as well as their relative intensities. Therefore, the appearance of these IR bands in the 800-1250 cm^{-1} region is a good indication of the presence of MTBE oxygenate in petrol.

Conclusion

In the present work petrol samples obtained from different filling stations within Aizawl city wereanalysed for the presence of oxygenate using FTIR-ATR technique in the mid IR region. From a total of 9 samples tested including premium quality the sample from Ruatkima filling station is found to contain MTBE. The presence of the oxygenate in petrol is identified from its distinct IR absorption bands at 1203, 1085 and 852 cm^{-1}due to the C-C and C-O vibrational modes of the molecule. Presence of oxygenate in petrol is good for engine as it reduces the exhaust emission level and increases engine output power.

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