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Fourier transform-infrared spectroscopic characterization of the particulate phase of commercial tuibur

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ABSTRACT

Tar is the term applied to the particulate phase of the tobacco smoke that gets collected on the cigarette filter during smoking, while it gets settled during the manufacture of tuibur. The particulate phase of tobacco smoke contains mainly relatively non-polar organic substances that are described as semivolatile and non-volatile constituents. Identification of toxic and carcinogenic compounds present in smokeless tobacco products such as tuibur is a preliminary step in assessing adverse effects associated with its consumption. Characterization of the molecular vibrational frequencies of various semivolatile and non-volatile chemical components associated with the tar phase of tuibur was performed using FTIR spectroscopy to ascertain these organic components.

Key words: Tobacco Smoke; Particulate Phase; Infrared Spectroscopy; Semiquinone; Poly Aromatic Hydrocarbons.

INTRODUCTION

Cigarette smoke is a highly complex aerosol consists of a broad range of chemical species distributed between the gas and the particulate phases.^{1,2} Cigarette smoke can exert cellular oxidative stress leading to adverse health effects more akin to smoke exposure including atherosclerosis, cancer and chronic obstructive pulmonary disease (COPD).³ The particulate phase contains dense microscopic droplets that con-

dense into particles (semivolatile and non-volatile tobacco constituents without water and nicotine) with size ranging from 0.1-1.0 μ m that normally gets trapped in the filter of cigarette. The trapped particulate phase can be virtually dissolved (95-98%) either using non-polar organic solvents and/or water.^{4,5}

The cigarette smoke is a very complex mixture that mainly consists of non-polar and polar compounds that can be studied in a rapid manner, simultaneously in real-time (as and when generated) as admixture of gas-phase compounds using FTIR spectroscopy as every gas exhibits its own information rich 'fingerprint' or characteristic vibrational spectral features.⁶ In-

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frared spectroscopy exhibits fingerprint specificity that enables the detection of individual species in a mixture of compounds with similar polarity and their associated specific functional groups.⁷ Fourier transform infrared (FT-IR) spectroscopy as a non-destructive molecular spectroscopic tool provides an opportunity to study, in a chemically informative way, the molecular specific (rather bond specific) information by identifying specific molecular vibrations as vibrational absorption bands associated with specific functional groups of diverse organic compounds present in a sample with multiple components.^{8,9}

In the present study, we attempted to describe the identification of tobacco-derived thermal degradation products that are semivolatile and nonvolatile products in tobacco smoke by employing FTIR spectroscopy. In addition, these products are relatively less polar besides they are insoluble in water more akin to that of the particulate phase of cigarette smoke, settle at the bottom of the container during the manufacture of tuibur¹⁰ and detected in the containers of commercially sold tuibur that may be unintentionally consumed along with tuibur solution by tuibur consumers.

MATERIALS AND METHOD

Tar sample was collected at a manufacturing site in the College Veng area of Aizawl City. Fourier transform infrared spectroscopy (FTIR) analysis of tar was carried out on a Thermo Avatar 370 FTIR spectrometer. A small quantity of tar sample was added to KBr in the ratio 1:80 approximately. The resulting matrix was ground for 5 minutes using mortar and pestle to obtain the uniform distribution of tar in KBr matrix. The fine powder was transferred into 13 mm diameter die and made into a neat pellet using a hydraulic press by applying a pressure of 7 ton/sq. mm. The resulting thin and semi-transparent pellet was subjected to FTIR analysis using an universal pellet holder. Infrared spectral data were collected over a range of 4000-400 cm^{-1} with an interferogram of 36 scans.

RESULTS AND DISCUSSION

For tar sample, the vibrational bands of certain functional groups appeared at similar locations in the spectrum, yet the sp^2 - and sp^3 - C-H valence band region at 3100-2800 cm^{-1} is much more detailed when compared with the FTIR spectrum of tuibur sample.¹⁰ In fact, The sp^2 C-H stretching vibrational frequencies between 3075 and 3000 cm^{-1} appeared as remarkably weak band (Figure 1) that is clearly visible and it is attributed to the typical aromatic C-H stretching vibrational band, while it was followed by many sp^3 -aliphatic C-H bond stretching vibrations in the region 2975-2850 cm^{-1} .¹¹ The observed sp^2 C-H valence vibration bands are characteristic vibrational features of poly aromatic hydrocarbons (PAHs).

While, residual humidity in the sample could enable intermolecular hydrogen bonding interactions between semiquinone species and / or carboxylic acid group which is detected as a broad and unstructured vibrational feature centered at 3375 cm^{-1} . The broad stretching vibrational band of O-H group is predominantly overlapping with the sp^2 C-H stretching vibrational band (Fig. 1). It is interesting to note that tar or particulate phase of cigarette smoke, similar to the tar phase of tuibur, is also known to exhibit free radical signal assigned to stable organic radical species in ESR spectroscopy arising due to the presence of free radical species associated with dihydroxy benzene moiety.^{4,5}

The distinctly sharp and rather dominant vibrational band at 1456 cm^{-1} (Fig. 2) is most likely due to C-H deformation (scissoring mode) that is more akin to that seen in CH_2 bending mode of saturated CH_2 bonds of long alkyl chain fatty acids.⁹ We also note that alkanes, alcohols and fatty acids are the key building blocks of the cell wall as the plant cuticles are reported to contain mainly lipids such as triterpenoids along with other long cuticular waxy (alkanes, alcohols and fatty acids) components.¹⁵ Moreover, aliphatic C-H deformation bands^{11,16} appear as weak shoulder bands at 1430 and 1370 cm^{-1} (symmetric bending mode) overlaid by the

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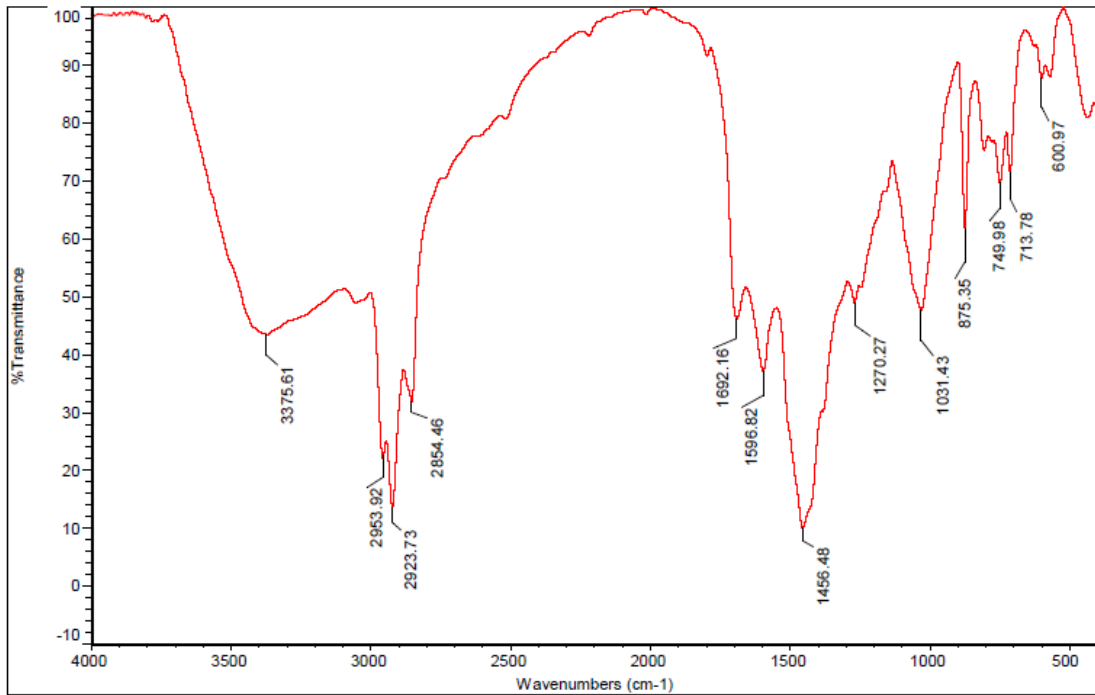


Figure 1. FTIR spectrum of tobacco smoke tar.

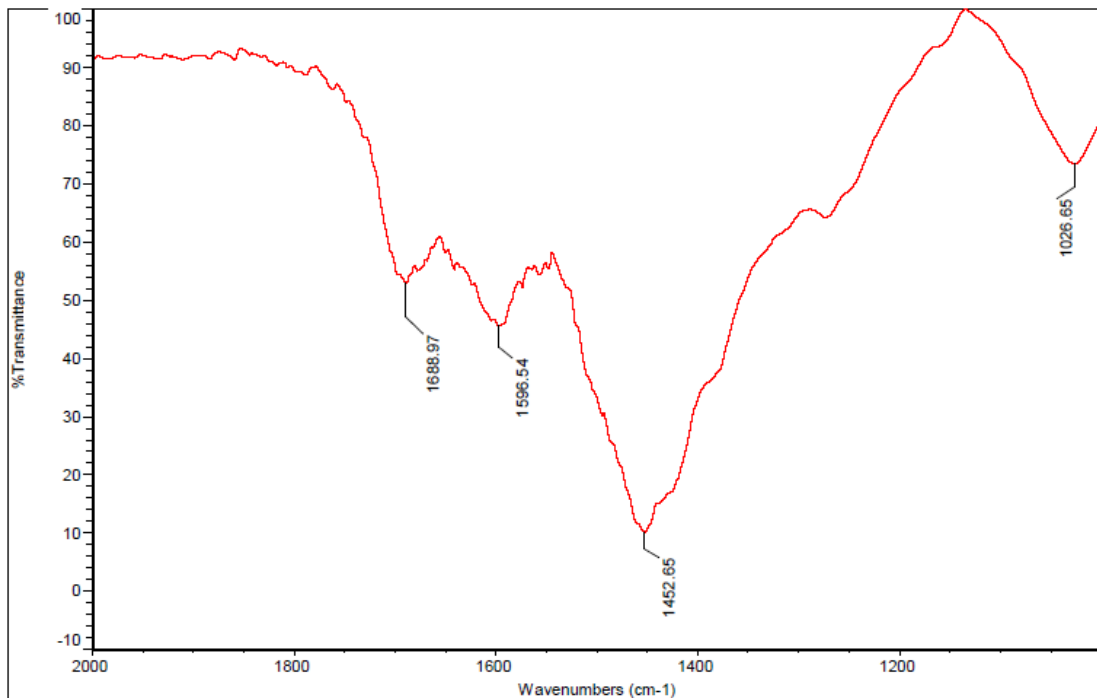


Figure 2. FTIR spectrum of tar in 2000-1000 cm⁻¹ region.

dominant 1456 cm^{-1} band. In the fingerprint region, evidently a weak vibrational band observed at 1270 cm^{-1} may be likely due to the presence of the C-O-C vibration, of possibly aromatic ether, while the weak aromatic overtone vibrations in the region of 2000 and 1800 cm^{-1} can hardly be detected.

In addition, in the functional group region for the double bond vibrations, at 1800 - 1500 cm^{-1} region, one would expect carbonyl ($\text{C}=\text{O}$) as well as the aromatic $\text{C}=\text{C}$ vibrations. In fact, The $\text{C}=\text{C}$ stretching vibrational bands of aromatic ring, skeletal vibrations involving $\text{C}=\text{C}$ bonds of the aromatic ring, such as polyaromatic hydrocarbons appear at their usual location between 1575 and 1625 cm^{-1} , i.e., at 1597 cm^{-1} rather as a sharp band. Perhaps, the interesting as well as surprising observation was that the $\text{C}=\text{O}$ stretching vibration band, clearly separated from $\text{C}=\text{C}$ vibrations, displayed at 1692 cm^{-1} as distinctly sharp band (Fig. 2). In addition to various PAHs, cigarette smoke is also reported to consist of free fatty acids ($\text{C}=\text{O}$ stretching \sim

1700 cm^{-1}) and semiquinone species ($\text{C}=\text{O}$ stretching $\sim 1650\text{ cm}^{-1}$).^{12,17} However, the observed carbonyl group vibrational band is rather low for a carboxylic acid functional group and slightly high for a quinone group.

In the fingerprint region, a rather intense peak at 1031 cm^{-1} is assigned to C-O stretching vibration that commensurates with the observation of $\text{C}=\text{O}$ vibrations (at 1692 cm^{-1}) in the functional group region.¹⁸ On the contrary, the C-O band could also be attributed to the presence of fatty acid and/or alcohol/semiquinone species as indicated earlier, the unusually broad and intense vibrational feature observed at 3375 cm^{-1} assigned to O-H group.^{11,19} Alternatively, the 1031 cm^{-1} band could also be assigned to the aromatic $=\text{C}-\text{H}$ in-plane deformation (bending) vibrations that is in agreement with the observation of other vibrational bands observed in the present study as well as reported in the literature.^{7,18-21} Furthermore, the fingerprint region is also very much sensitive to subtle steric or electronic effects due to the nature of substituents

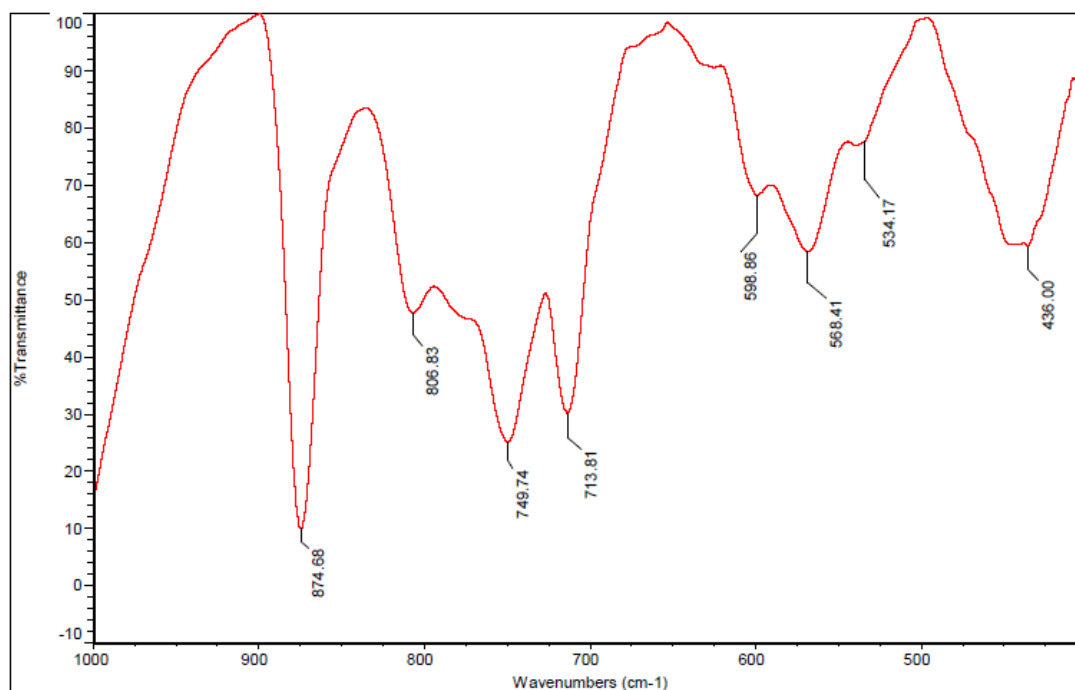


Figure 3. FTIR spectrum of tar in the range of 1000 - 400 cm^{-1} .

and it will reflect in the concomitant shift in the position of vibrational bands. It seems likely that aromatic =C-H in-plane deformation (bending) vibrations could also be assigned to 1270 cm^{-1} band^{7,20} as tar phase / particulate matter of cigarette smoke contains more than 1000 multifarious chemicals including a range of aromatics with varying degree of nonpolarity.

In the long wavelength region (900-600 cm^{-1}), there were many peaks observed for the tar sample as displayed in Figure 3. A sharp and intense peak distinctly observed at 875 cm^{-1} is attributed to the para-substituted aromatic compound(s). In addition, vibrational bands were observed at 806, 780, 750 and 714 cm^{-1} , indicative of the pattern of substitution in the aromatic ring, correspond to para-, ortho-, and meta-substituted aromatic compounds, respectively as meta-substituted aromatic compounds generally exhibit split bands in the low-frequency region.^{7,19} Any further attempt at explanation at this stage would be purely speculative and premature due to the limited data available and it is obvious that further experimentation is certainly needed.

The observation of vibrational bands associated with various aromatic compounds along with the polyaromatic hydrocarbon compounds commensurate with the non-polar nature of tar phase which gets separated from the aqueous phase during the manufacture of tuibur. Both redox-active and redox-inactive metal species are present in the particulate as well as gas phase of cigarette smoke and they can potentially exert oxidant burden that may be partially responsible for the toxicity of these metals.²² Trace amounts of heavy metal ions, both redox-active and redox-inactive metal species, in the tar of cigarette smoke are notable because of their capacity to form coordination complexes with many of the organic molecules present in the particulate phase condensate.^{23,24}

CONCLUSION

In summary, the FT-IR method presented here is an attempt to provide more or less gener-

alised picture of the putative chemical environment in addition to potential risk factors that may be present in the tar phase of commercial tuibur. However, the utilization of additional molecular spectroscopic methods of structural analysis such as NMR, Mass spectrometric methods would be beneficial to gain further understanding of the structural and molecular aspects of the tar phase of tuibur solution. Although we have not completely determined the complete chemical composition of tar phase of tuibur, albeit we can surmise that the presence of polyaromatic hydrocarbons and carbonyl compounds present in the tar phase may also contribute to the increased incidence of cancer when inadvertently consumed by the tuibur users.

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