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Identification of Physical Clues by FTIR Spectroscopy

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ABSTRACT

Infrared spectroscopy is now well established as a basic technique for the qualitative and quantitative analysis of several compounds. The range of applications of vibrational spectroscopy is very wide. It has been proposed in the present study to highlight the application of the infrared spectroscopy in the field of forensic science. The accuracy of the present investigation is enhanced by Fourier transform infrared spectroscopy. Here in this investigation internal standards calculation technique is used to identify the physical clues of various commodities at the crime spot. The reliability of this method has been tested using a model experiment. Identification of correct physical clues of a substance is used to prevent fraudulent insurance claim.

Keywords: Physical clues, Forensic, Arson, Cyclo-alkenes, Leucine, Valine, Protein, Internal standard, PACS Nos: 33.20Ea, 33.10Gx,33.20Fb,33.20Tp.

INTRODUCTION

Modern society is harmed by crimes which pose a serious threat to the peace, property and comfort of the people. Quality of life is seriously affected by overall crimes. Quality Town or city is judged according to the minimum crime rates. One among that is arson. The malicious burning of a Public property has been recognized as a serious crime. In every protest in Africa there is torching of public property. In recent years the incidence of arson in many countries has reached a level of national concern. According to statistics, there are numerous motives for arson, one among that is fraudulent claim of insurance[1]. The remains and residues at the scene is very important.

In the story of fraudulent claim of insurance, fire accelerants are used to accelerate fire rapidly. The remains at the site may contain this fire accelerants. The fire accelerant is used to erase the finger print of remains. In order to combat this type of crimes and to identify the truth behind the clues, various advanced and sophisticated instrumentation techniques are needed. Now a days forensic chemistry is widely used. Forensic chemistry is that field of knowledge which involves the application of the principles of chemistry and related sciences to the examination of physical evidence collected at the scene of a crime and the presentation of results of the examination in a court of law or public forum an expert witness, a forensic chemist who has either performed or supervised the tests. The forensic chemistry has facility of applied analytical chemistry with increasing emphasis on trace analysis employing various analytical and modern technique[2-5]. The task of the forensic chemist is to analyze the physical evidence found at the scene of crime. The objective either to provide information that may link a suspect with the evidence collected at the scene of crime or to answer questions about crime. The present FTIR technique is used to find crime with novelty. In the first part of the study, FTIR spectroscopy has been successfully applied in the identification of type of oil found at the scene of crime (test sample) and the second part of the study investigates identification of perishable commodities like cashew, ground nut and paddy. In this method, the absorbance ratios among the selected fundamental bands of source sample have been calculated and compared with the test samples. Comparison between internal standards for the source and the test samples enable us to finger print the samples collected from scene.

EXPERIMENTAL

Cloths stained with oil collected from the crime spot (test sample) and immersed in the solvent carbon tetrachloride (CCl_4). The pure stained oil is obtained after the evaporation of solvent. The oil thus extracted from cloths is collected on micro-glass plate. The spectra are recorded over a region of 400-4000 cm^{-1} using BRUKER IFS 66V Double beam Spectrophotometer under identical conditions.

The Fourier transform infrared spectra of the samples of Cashew, groundnut and paddy in the form of ash have been derived from reliable source as reference sample. They are presented in Figs.1-3 respectively. The samples of charred residues of the commodities (test sample) collected from place of arson have been examined carefully. The observed FTIR spectra of these test samples are presented in the same Figs.1-3 respectively for comparison. All Spectral measurements of the samples of commodities have been carried out in BRUKER 66V Double beam Spectrophotometer in the range 400-4000 cm^{-1} under identical conditions.

RESULTS AND DISCUSSIONS

Oil Sample

The oil sample collected from the crime spot (test sample) consists of mixture of hydrocarbon oils. The hydrocarbon oils are complex mixture of alkanes and cycloalkenes. The unsaturated hydrocarbons, alkenes are obtained on a large scale in hydrocarbon oils.

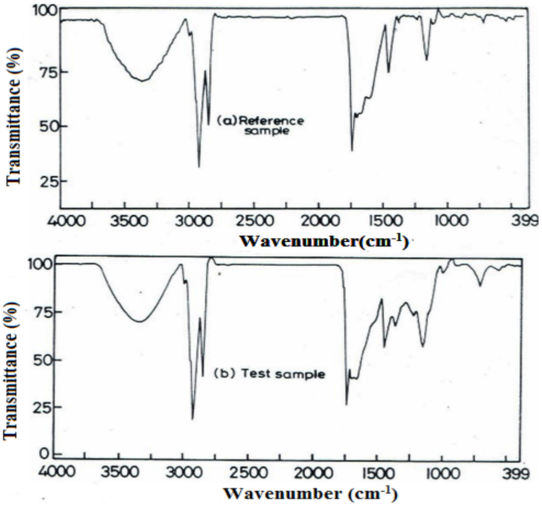

Fig. 1. FTIR Spectra of Cashew

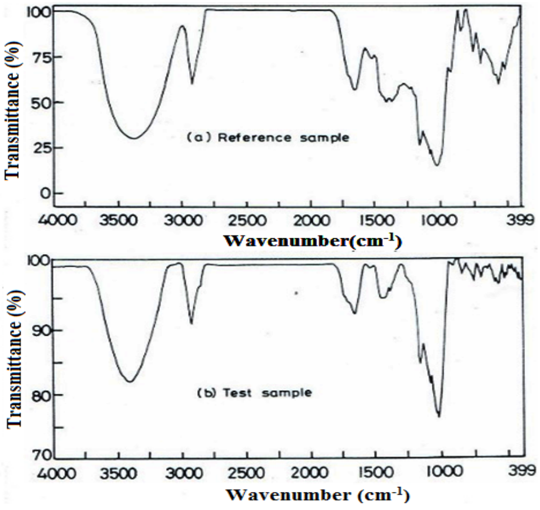

Fig. 2. FTIR Spectra of Ground Nut

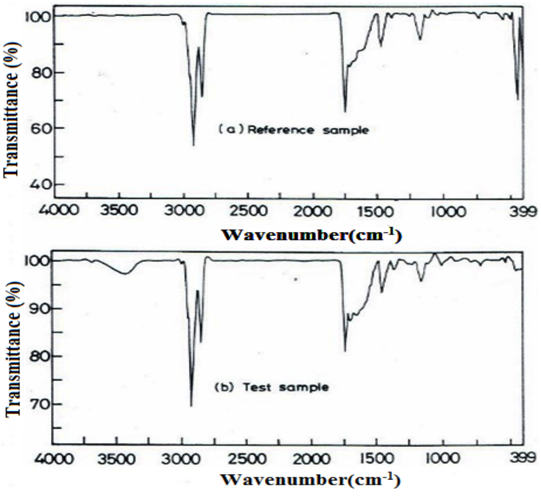

Fig. 3. FTIR Spectra of Paddy

The most of the saturated hydrocarbon oil will contain absorptions due to symmetric and anti-symmetric $–CH_2$ stretch, symmetric and anti-symmetric $–CH_3$ stretches. The spectra of the most of the hydrocarbon oils shows shoulder bands or a doublet at around 2900 cm^{-1}. Hence, a sharp band found at 2971 cm^{-1} is assigned to C-H stretching of methyl group. C-H stretching of methylene group is found at 2923 and 2853 cm^{-1}. The C-H bending vibrations of saturated hydrocarbons is found over a region of 1320-1480 cm^{-1}. Hence, the band found at 1462 cm^{-1}, 1450 cm^{-1} and 1377cm^{-1} are attributed to $–CH_3$ and $–CH_2$ deformation respectively[6]. The rocking and the wagging vibrations give absorption which are of little value expect when four or more consecutive methylene group occur in an open chain. The compound containing such a feature generally show broad band near 720 cm^{-1}, is attributed to out-of-plane C-H vibration. In the present investigation, various band observed at characteristic position of the hydrocarbon oil are assigned and presented in the Table 1.

Table 1: Vibrational Band Assignments of Oil under Test

Frequency (cm^{-1})		Assignment
2971	2971	C-H stretching of Methyl group
2923	2920	C-H stretching of methelene group
2853	2853	C-H stretching of methelene group
1462	1460	CH_3 deformation
1450	1452	CH_3 deformation
1377	1377	CH_2 deformation
722	722	Long chain $–CH_2$- Out of plane deformation

The Fourier transform infrared band assignments of various vibrations observed in the spectra of the charred remains of the samples are in respect of their content in them. The charred remains of the samples contain valuable complex nitrogenous organic compounds, carbohydrates and traces of lipids.

Cashew

The Cashew contain important nitrogenous compound called proteins. The proteins may be considered as polypeptides of high molecular weight and composed of hundreds of biological important alpha amino acid units. These alpha amino acids are ingredient of food occur in plants. Susheela and Pruthi[7] had identified a good quality of proteins in cashews. They have also identified some important amino acids like leucine, valine, alanine, protein, serine and aspartic acid. The FTIR Spectra of charred cashew show the important protein vibrations. Primary amino-acids are characterized by NH^{3+} stretching band in the 3100 -2600 cm^{-1} region. This broad band may be due to superimposing of O-H stretching of phenolic ingredient of cashew[8] and NH_3^+ stretching[9]. In the present investigation. N-H stretching is superimposed by O-H stretching vibrations. Hence, a broad band is appeared at around 3360 cm^{-1}. Strong bands appear at around 3000 cm^{-1} are attributed to aliphatic C-H stretching vibrations of methyl and methylene group in the amino acid. In the spectra of charred cashew N-H bending vibration appear as a broad band in the region 1600-1650 cm^{-1}. Hence a band a 1673 cm^{-1} and 1550 cm^{-1} are assigned to anti-symmetric and symmetrical N-H bending vibration respectively. Hydro-chlorides of alpha amino-acids show strong carbonyl absorption at 1755-1730 cm^{-1} [9,10]. In the present investigation, Carbonyl absorption is observed at 1745 cm^{-1} in both of the samples. A sharp band found at 1163 cm^{-1} may be due C-C-O stretching vibration[9]. The N-H oscillation (torsional oscillation) is found at 723 cm^{-1}. In the present investigation, the assignments are made in accordance with the content present in them and are given in the Table 2. Both the spectra of charred and uncharred cashews dis play similar vibrational bands.

Table 2: Vibrational Band Assignments of Ingredients of Cashew

Frequency cm^{-1}		Assignment
3379 (s)	3361(s)	O-H stretching vibration
2924 (v)	3005 (v)	C-H stretching
2853 (vs)	2854(vs)	Aliphatic C-H stretching of methyl and methelene group
1745 (vs)	1745 (vs)	Aliphatic C-H stretching methyl and methelene group
1709 (m)	1708 (m)	Carbonyl absorption of amino acids
1650 (m)	1673(m)	Carbonyl absorption of amino acids
1600 (m)	1550 (m)	Anti-symmetrical NH_3^+ bending
1461 (m)	1460 (m)	2X723
1377 (vw)	1377 (vw)	C-H bending of methyl and methelene group
1238 (vw)	1238 (vw)	2925-1673
1163 (m)	1163 (m)	
		C-C-O stretching
722 (vw)	723 (vw)	Torsional Oscillation of NH_3^+ group

Ground Nut

The constituents of ground nut are investigated by many researchers[11,12]. Ground nut contain fatty acids[12] called neutral fatty acids. These fatty acids are simple triglycerides are major components of depot or storage fats in plants. In plants the highest concentration of fats are found in specialized tissues such as those of seeds or fruits, where they act as an energy reserve. It is also found that it contains proteins in the form amino acids[11]. The spectra of charred remains of groundnut show systematic band as their constituents at characteristic positions. The spectra of various amino acids show NH_3^+ stretching absorption in the region 3100-2600 cm^{-1} [9]. In the present investigation, the band observed at 3006 cm^{-1} is attributed N-H stretching of amino acids in the charred remains of the sample. Bands of very sharp intensity observed at 2924 cm^{-1} and 2853 cm^{-1} are assigned to aliphatic C-H stretching of methyl and methylene present in amino acids (or) non destructed traces of fatty acids present in the sample. The new band arises at around 3455 cm^{-1}(Fig. b) may be due to partially charred sample taken for the test. In the present investigation it has been attributed as O-H stretching vibration of wet remains in the sample.

Usually, in the peptide bonds carbonyl vibration occur in the region 1660-1690 cm^{-1} [9, 10]. The frequencies themselves are characteristic of hydrogen bonded –C=O and –N-H group and are displaced typical of the free groups. The C=O absorption maxima for hydrogen bonded group is found at 1660 cm^{-1} and C=O absorption maxima for non-hydrogen bonded group found at 1695 cm^{-1}. In the spectra of ground nut, the carbonyl absorption maximum is found at high frequency region (at 1745). Hence it can be decided that the proteins in groundnut belong to beta structure, where stretching vibrations are oriented perpendicular to the axis of the molecules. In the spectra of ground nut, N-H bending vibrations are found at 1660 cm^{-1} and 1575 cm^{-1}. A band of strong –to-medium intensity found at 1164 cm^{-1} in both of the groundnut samples is assigned to C-C-O stretching[9]. The assignment of bands are presented in Table 3.

Paddy

Paddy contains good quality of proteins. It was identified that it contains the important amino-acids like threonine, isoleucine and valine[11], It contains a rich amount of carbohydrates. The most of the bands obtained for the charred paddy are identified as fingerprints of various amino-acids present in the sample. A strong band appeared at 3409 cm^{-1} is assigned to O-H stretching Amylose and Amylopectin present in the carbohydrates. N-H stretching of amino acid present in the sample is augmented by O-H stretching vibration. A band of moderate intensity found at 2924 cm^{-1} may be due to aliphatic C-H stretching of methyl and methylene group present in the sample[9]. Alpha amino hydro chlorides absorb strongly in the region 1755-1730 cm^{-1} [9,10] is due to carbonyl absorption. In the present investigation, carbonyl absorption is found at 1661 cm^{-1} and superimposes on N-H bending vibrations. The assignment of various vibrational bands found in the spectra of paddy are presented in the Table 4.

Table 3: Vibrational Band Assignments of Ingredients of Groundnut

Frequency (cm^{-1})		Assignments
-	3455 (V)	May be due to wet remains of the sample
3006 (V)	3007 (V)	N-H stretching
2924 (S)	2924 (VS)	Aliphatic C-H stretching of aminoacids
2853 (M)	2853 (M)	Aliphatic C-H stretching of aminoacids
1745 (S)	1745 (S)	Carbonyl absorption
1709 (M)	1708 (M)	Carbonyl absorption
1650 (M)	1660 (M)	N-H bending
1600 (M)	1575 (M)	N-H bending
1461 (M)	1461 (M)	2x724
1377 (V)	1377 (V)	C-H bending
		O
		II
1164 (M)	1164 (M)	C-C-O stretching
1100 VW)	1116 (V)	2853-1745
723 (VW)	724 (V)	Torsional oscillations of amino group

Table 4: Vibrational Band Assignments of Ingredients of Paddy

Frequency (cm^{-1})		Assignment
3374 (VS)	3409 (VS)	O-H stretching of Amylose/Amylopectin present in stretch/ N-H stretching
2925 (S)	2924 (S)	aliphatic C-H stretching
1658 (S)	1661 (S)	carbonyl vibrations of amino-acid
1517 (M)	1538 (V)	N-H bending
1414 (M)	1457 (M)	N-H bending
1370 (M)	1383 (M)	C-H bending
		O
		II
1154 (M)	1155 (M)	C-C-O stretching
1078 (M)	1080 (M)	C-H out-of-plane bending
1024 (S)	1022 (S)	C-H out-of-plane bending
929 (V)	918 (V)	C-H out-of-plane bending
762 (V)	762 (V)	N-H Torsional oscillations of amino group
708 (V)	709 (V)	C-H out-of-plane bending

Finger Printing of Source and Test Samples

For the identification of the test samples collected from the suspected spot, the absorbance values of some prominent bands observed in the reference samples are calculated. The absorbance ratios among the bands observed have been computed for the reference and the test samples are presented in Table 5. If both the samples are identical, the ratios of absorption at various band position would compare well. Otherwise the ratio at different band position would be different.

Table 5: Comparative Study on the Internal Standards of Reference and Test Samples

Sample : Oil

Wave No.	2923(2923)	2853 (2853)	2724 (2728)
2923 (2923)	1.0000	1.4660 (0.5453)	0.2939 (8.0539)
2853 (2853)	0.8532 (1.8338)	1.0000	2.9030 (14.769)
2724 (2728)			1.0000

Sample : Cashew

Wave Number cm^{-1}	2925 (2924)	2854 (2854)	1746 (1745)	1461 (1461)	1163 (1163)
2925 (2924)	1	1.4374 (1.5662)	1.7692 (1.8055)	2.6538 (2.1666)	3.2857 (2.6000)
2854 (2854)	0.6956 (0.6384)	1	1.2307 (1.1527)	1.8461 (1.3833)	2.2857 (1.6599)
1746 (1745)	0.5652 (0.5538)	0.8124 (0.8674)	1	1.4999 (1.1999)	1.8571 (1.4399)
1461 (1461)	0.3768 (0.4615)	0.5416 (0.7228)	0.6666 (0.8333)	1	1.238 (1.2000)
1163 (1163)	0.3043 (0.3846)	0.4375 (0.6024)	0.5384 (0.6944)	1	0.8076 (0.8333)

Sample : Groundnut

Wave Number cm^{-1}	3007.6 (3006.7)	2924.4 (2924.8)	2853.7 (2853.9)	1745 (1745.6)	1461.5 (1461.5)	1164.7 (1164.3)	724.8 (723.2)
3007.6 (3006.7)	1	0.0392 (0.0579)	0.0796 (0.0999)	0.0786 (0.1020)	0.1579 (0.1999)	0.2500 (0.2285)	0.7500 (1.3333)
2924.4 (2924.8)	25.4983 (17.2503)	1	2.0291 (1.725)	2.0131 (1.7602)	4.0262 (3.4499)	6.3748 (3.9428)	19.1246 (23.0001)
2853.7 (2853.9)	12.5658 (10.0001)	0.4928 (0.5797)	1	0.9921 (1.0204)	1.9841 (1.9999)	3.1416 (2.2857)	9.4248 (13.3333)
1745 (1745.6)	12.6658 (9.8001)	0.4967 (0.5681)	1.0070 (0.9799)	1	1.9999 (1.9599)	3.1666 (2.24)	9.4998 (13.0666)
1461.5 (1461.5)	6.3329 (4.3750)	0.2483 (0.4374)	0.5039 (5.0000)	0.5000 (0.5102)	1	1.5833 (1.1428)	4.7499 (6.6667)
1164.7 (1164.3)	3.9998 (4.3750)	0.1568 (0.2593)	0.3183 (0.4464)	0.3157 (0.4464)	0.6315 (0.8749)	1	3.0000 (5.8333)
724.8 (723.2)	1.3332 (0.7500)	0.0522 (0.0434)	0.1061 (0.0749)	0.1552 (0.0765)	0.2105 (0.1499)	0.3333 (0.1714)	1

Sample : Paddy

Wave Number cm^{-1}	2925 (2924)	1661 (1658)	1023 (1025)	762 (762)	710 (708)
2925 (2926)	1	(1.0373) (1.1562)	0.5964 (0.7872)	2.1176 (2.1764)	4.857 (2.6428)
1661 (1658)	0.964 (0.8648)	1	0.575 (0.6808)	2.6418 (1.8623)	4.6824 (2.2857)
1023 (1025)	1.6764 (1.2702)	1.7389 (1.4687)	1	0.3330 (2.7647)	8.1426 (3.3571)
762 (762)	0.3647 (0.4594)	0.2745 (0.3312)	0.1579 (0.3617)	1	1.2857 (1.2142)
710 (708)	0.2058 (0.2783)	0.2135 (0.2375)	0.1228 (0.1978)	0.7777 (0.8235)	1

The values in the paranthesis refer the internal standards for test sample.

CONCLUSION

Forensic chemistry is the field involves the application of the physical chemistry and related sciences to the examination of physical evidence collected at the scene. In order to present the results of the examination in a court of law, forensic chemist needs sophisticated instrument techniques like Fourier Transform Infrared Spectrophotometer and UV-Visible Spectrophotometers. The assignment of characteristic vibrational frequencies found in the spectra of the samples under test and the calculation of internal standards of the known and unknown samples, become a scientific proof for the physical evidence of things found at the scene of crime.

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Conflicts of Interest

The authors declare no conflict of interest.

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