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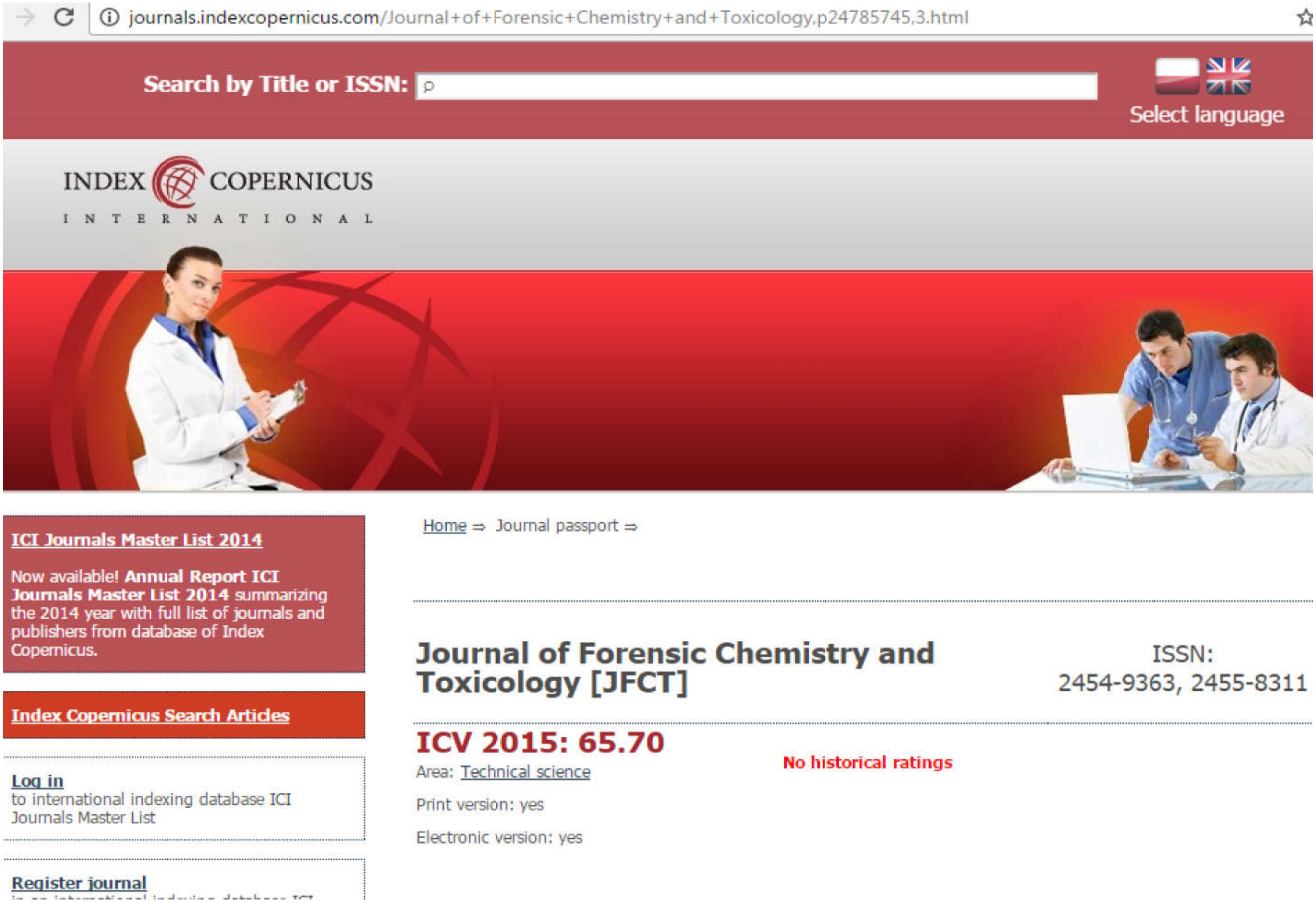

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Original Article

Prediction of Survival using TRISS in Train Accident Victims in Tertiary Care Hospital Delhi

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Abstract

Evaluation of trauma and prediction of outcome in 255 train accident victims in Delhi was studied out of which 40 cases survived and taken up for this study. Trauma and Injury Severity Score (TRISS) was calculated and its correlation with period of survival was determined. Males and females were 86.7% and 13.3% respectively. Mean age was 37.5 years. Most common age group involved was 21–30 followed by 31-40 years. The region of the body most commonly involved in survivors was the lower limbs followed by upper limbs, head and chest while in the victims who died was head followed by chest and abdominal injury. Thirty percent of the survivors belonged to TRISS group 50-80 followed by 70% survivors to TRISS >80 group. There was a positive correlation between TRISS and probability of survival.

Keywords: Trauma and Injury Severity Score (TRISS); Abdominal injury; Limbs.

Introduction

Railways were first introduced in India in 1853. By 1947, the year of India's independence, there were forty-two rail systems. In 1951 the systems were nationalized as one unit, the Indian railways, becoming one of the largest networks in the world. The Indian railways have 115,000 kilometers of total track over a route of 65,808 kilometers and 7,112 stations. It has the fourth longest railway network after those of the United States, Russia and China. In India in 2014, 2,547 Railroad (Railway crossing) accidents were reported in which 2,575 deaths occurred, comprising 2,186 males, 388 females and 1 transgender. During this period other Railway accidents reported were 28,360 in number in which 25,006 deaths occurred, comprising 21,407 males, 3,587 females and 12 transgender. In Delhi in 2014, 11 Railroad (Railway crossing) accidents were reported in which 11 deaths occurred, comprising 9 males and 2 females. During this period other Railway accidents reported were 914 in number in which 856 deaths occurred, comprising 764 males and 92 females. (There were no transgender deaths in Delhi) [1,2].

Rail road accidents are those train accidents which occur on unmanned/manned crossings when people try to cross the railway track, and all the other types of train accidents are categorized in the other Railway accidents i.e. passengers falling off the roof of moving trains, falling while entering or alighting from moving trains or falling off the platform or crossing the railway track at places other than railway crossing and being struck or run over by trains.

Trauma related to railway accident victims is usually severe, instantly fatal and extremely mutilating. Certain features such as wheel marks on the body, dirt and grease contamination and the manner of severance of tissues deserve special observation to rule out criminal violence [1].

Various scores are available for measuring severity of injuries in trauma victims like, Abbreviated Injury Scale (AIS), Injury Severity Score (ISS), New Injury Severity Score (NISS), Trauma and Injury Severity Score (TRISS) and Revised Trauma Score (RTS).

The TRISS is a composite of the ISS, Revised Trauma Score (RTS), and age. It has great predictive value but its widespread applicability is limited because it is difficult for many trauma facilities to compute because it requires 8 to 10 variables [3].

Material and Methods

1. Material for the present study was collected from the cases of train accidents brought to the Mortuary of Department of Forensic Medicine for Medico-legal autopsy and Casualty of a Tertiary care hospital, Delhi.
2. Cases of train accidents brought during the period November 2010 to February 2012 were taken up for the study. A total of 255 cases were studied irrespective of age and sex of victims, of which 40 cases were discharged from the hospital after appropriate treatment and rest died due to fatal train accident injuries.
3. The severity of the injuries has been established using the NISS. NISS of each injured body region have been calculated using the Association for Advancement of Automotive Medicine, latest protocol 2005 [2].
4. NISS along with Glasgow Coma Scale (GCS), Systolic Blood Pressure (SBP) and Respiratory Rate (RR) have been used to calculate Trauma and Injury Severity Score (TRISS) in victims surviving the railway accidents by using TRISS calculator which determines the probability of survival from the ISS, RTS and patient's age. ISS and RTS scores can be inputted independently or calculated from their base parameters.
5. Dead bodies showing severe degree of decomposition particularly of the internal organs have been excluded from this study to avoid false interpretation of findings.
6. Detailed information regarding manner of incidence and the category of victims was obtained from inquest papers, police, and relatives of the deceased. Victims were categorized as pedestrians, vehicular occupants, train occupants, falling from the door of moving trains and falling from the roof of the moving trains.
7. Consent for the participation in the study has been taken from victims/ relatives of deceased.
8. The Patients/ next of kin were informed about this study, methodology to be used and why this study was necessary in this region.

In patients surviving the train accidents, information was also obtained from the hospital case records of the admitted patients.

Results

Cases of train accidents brought during the period November 2010 to February 2012 were taken up for the study. A total of 255 cases were studied irrespective of age and sex of victims, of which 40 cases survived and discharged from the hospital after appropriate treatment and rest died due to fatal train accident injuries. Of the total 40 survivors involved in train accidents, the results are as follows-

Age Incidence

In the victims, most common age group involved was between 21-30 years of age comprising 49% of cases followed by 31-40 years age group comprising 31% of cases. Victims of >60 years age comprised only 2% cases and there was no victim below 10 years of age (Table 1, 2).

Table 1: Age distribution of Survivors

Age groups in year	Males	Females	Total	Percentage
0-10	00	00	00	0.0
11-20	04	01	05	12.5
21-30	18	01	19	47.5
31-40	08	01	09	22.5
41-50	01	02	03	7.5
51-60	01	01	02	5.0
>60	01	01	02	5.0
TOTAL	33	07	40	100

Table 2: Sex distribution in Survivors

Age group in years	Males	Percentage	Females	Percentage
0-10	0	0	0	0
11-20	4	12.12	1	14.29
21-30	18	55.55	1	14.29
31-40	8	24.24	1	14.29
41-50	1	3.03	2	28.57
51-60	1	3.03	1	14.29
>60	1	3.03	1	14.29
TOTAL	33	100	7	100

Duration of Hospital Stay

In 40 total survivors, the duration of stay in hospital was less than 24 hours in 7 cases and up to 3 days in 5 cases. Sixteen victims were in 72-168 hours group (3-7 days), and 12 victims were in >168 hours group (>7 days). Only one victim was in 0-6 hour's group (Table 3).

Table 3: Distribution of Survivors in relation to duration of stay in the hospital

Duration of hospital stay (in hours)	Survivors	%
0-6	01	02.5
6-12	03	07.5
12-24	03	07.5
24-72	05	12.5
72-168	16	40.0
>168	12	30.0
Total	40	100

Regions of Body Involved in Victims Surviving Train Accidents

Lower limbs were involved in 62.5% of victims, followed by involvement of upper limbs (55%). Head involvement was only in 5 victims (12.5%) and chest injuries were found in 9 victims (25%)(Table 4).

Table 4: Distribution of victims in relation to body regions involved

Body region involved	Survivors	%
Head	05	12.5
Chest	09	22.5
Upper limb	22	55
Lower limb	25	62.50

*Total exceeds 100% because more than one body region involved per victim.

New Injury Severity Score (NISS) in the Survivors

Maximum survivors (34) were found having NISS less than 25 while NISS 25-50 was seen in 05 victims and only one case was found in the NISS group 50-75 (Table 5).

Table 5: Distribution of victims in relation to NISS

NISS Groups	Survivors	Percentage
0-25	34	85.5
25-50	05	12.5
50-75	01	02.5

Probability of Survival

Twenty eight survivors out of 40, were found to have a probability of survival >80 TRISS group (most cases were between 85-95%). 12 survivors were in between 50-80 TRISS group (most cases were between 70-80%) while no survivor was found in TRISS 0-50 group out of 50 victims. Probability of survival was measured in terms of TRISS value which is proved to be more accurate for penetrating then blunt injuries (Table 6).

Table 6: Distribution of victims in relation to TRISS

Triss	Survivors	%
0-50	0	00
50-80	12	30
>80	28	70

Table 6: Distribution of victims in relation to TRISS

Triss	Survivors	%
0-50	0	00
50-80	12	30
>80	28	70

Results showed a positive correlation between TRISS value and Ps (period of survival) with an *r*-value of -0.226 ($p < 0.001$) and Coefficient of a determination $r^2 = 0.051$. This means that as TRISS value increases period of survival increases.

Discussion

Age and Sex

Of the 40 victims who survived, the most common age group involved was between 21-30 years comprising 47.5% of cases followed by 31-40 years age group comprising 22.50% of cases. Victims aged more than 60 years age comprised only 5% cases. There was no victim below 10 years of age. A large number of cases in this study belonged to age group of 21-40 years (70%). This can be attributed to the fact that this age group has a high level of participation in outdoor activities and therefore is most vulnerable to trauma.

Among these 40 victims, males comprised 33, i.e. 82.5% of total cases, while females were only 7 in number, i.e., 17.50% of the total cases (Table 1, 2). Males being more involved in outdoor activities prefer railways as the cheap, quick and comfortable mode of transport for travelling from one place to another and are therefore more vulnerable than females. In the study of Howells et al [4], males were also the commonest victims (Table 7).

Table 7: Comparison of sex of survivors in different studies

Studies	Male	Female
Present study	82%	18%
Spaite et al[5]	90%	10%
Akkas[6]	68%	32%

In the study done by Spaite et al [5] among the 31 survivors out of total 41 victims 90% were men and the age ranging from 1 to 67 years (mean age = 31.2 years). The results of this study in relation to age and sex of the survived victims are in agreement with the results of the present study (Table 7, 8).

In the study done by Akkas et al [6] among the 37 survivors out of total 44 victims of train accidents 68 % were males and 32 % females. The mean age was 31.8 years. The results of this study in relation to age and sex of the survived victims are in agreement with the results of the present study (Table 8).

Table 8: Comparison of mean age in the victims between different studies

Studies	Mean age
Present study	37.5
Spaite et al[5]	31.2
Akkas[6]	31.8
Shapiro et al[7]	30.6
Davis et al[8]	39
Agalar et al[9]	32
Bhatti and Razak[10]	35.6

Similar findings were found in study of Prabhakar and Sharma [11]. Although the author has only considered the victims of train crashes whereas the present study took cases like pedestrians, persons falling from trains, where no train crashes were involved.

The present study differs from the study done by Rautji and Dogra [12]. The reason is, the study was done with smaller sample size including only South Delhi region, where very less numbers of train accidents were reported. Higher numbers of hospital deaths may be because the victims of train accidents hospitalized in South Delhi hospitals where most of the cases were referred cases from other hospitals.

Table 9: Comparison between different studies in relation to survival period

Survival period	Prabhakar and Sharma[11]	Present study	Rautji and Dogra[12]
Spot death	46 (30.86%)	40 (40%)	28 (22.01%)
0-6 hours	--	50 (50%)	71 (55.91%)
6-12 hours	--	06 (6%)	
12-24 hours	--	06 (6%)	
1-7 days	--	24 (24%)	
7-14 days	67 (44.97%)	14 (14%)	
14-60 days	29 (19.46%)	--	
>60 days	6 (4.03)	--	

Pattern of Injuries

In the victims who survived train accidents, lower limbs injuries were seen in a large number of cases (62.5%) followed by upper limbs injuries (55%). Head involvement was seen only in 5 victims (12.5%) and chest injuries were found in 9 victims (25%). The reason for higher involvement of the lower extremity may be due to the victim falling between the train and the elevated platform while boarding or deboarding the train.

All the victims showed associated external injuries. Most common external injuries were lacerations and abrasions**.**

In the study done by Akkas et al [6] among the 37 survivors out of total 44 victims of train accidents the most common region of the body involved was the lower extremity. 19 limb amputations were performed in 14 patients. This finding was in agreement with the present study.

New Injury Severity Score

Fourty victims (70%) were found in 0-25 NISS group, 18 victims (30%) belonged to 25-50 NISS group and 42 victims in the 50 – 75 NISS group. The reason is this group (50 -75) constitutes the serious and non survivable injuries.

The findings were also found Similar in study by Howells NR [4]. In their study, maximum victims (90.16%) were under <16 NISS group and 9.86% victims were in >16 NISS group.

Similar findings were found in study of Spaite et al[5]. In their study, maximum victims (75%) were under Injury Severity Score 15 and rest 25 % were above Injury Severity Score 15.

Duration of Hospital stay in Survivors

In 82.5% of survivors, the duration of stay in hospital was more than 24 hours (1 day). 16 victims were in 72-168 hours group (3-7 days), comprising 40% and 12 victims were in >168 hours group (>7 days), comprising of 30% of total victims. Only one victim was in 0-6 hour's group.

Table 10: Duration of hospital stay in survivors

Duration of hospital stay (in hours)	Number of victims	Percentage
0-6	1	2.5
6-12	3	7.5
12-24	3	7.5
24-72	5	12.5
72-168	16	40
>168	12	30
Total	40	100

Table 11: Comparison of TRISS in Different Studies

Studies	TRISS groups		
	<80	>80	>95
Present study	30%	70%	--
Howells NR[4]	--	100	--

Trauma and Injury Severity Score (TRISS) for the Survivors

The probability of survival was found up to 80% in 12 victims (30% of cases) and more than 80% in 28 victims (70% of cases) (Table 11).

Similar findings were found in study of Howells NR et al [4]. In both the studies maximum victims were in >80 TRISS group.

The finding in the survivors indicate that greater the TRISS value better the probability of survival. Hence, TRISS is a good prognostic indicator.

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Original Article

Retrospective Analysis of Pattern of Poisoning in Tertiary Care Hospital, Hapur; NCR Region

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Abstract

A retrospective study of 140 cases of poisoning received in the casualty of Rama Medical College Hospital and Research Center Hapur (Ghaziabad) Uttar Pradesh during a span of last 3 years (2014-2016) was done to know the socio-economic profile and pattern of acute poisoning in the region. All admitted and brought dead cases of acute, known and unknown poisoning, from all age were included in the study. Males and females were 62% and 38% respectively. Most common age group was 21-30 years and majority of victims were married. Most of the victims belonged to lower (33.6%) or lower-middle (60.7%) class. Organophosphate (37.1%) was the most common poisoning, followed by Celphos (21.4%) and other unknown poisoning (18.6%) responsible for more than two-third of the cases. Majority of poisoning cases (85.7%) were suggestive of suicide, of which family quarrel (31.7%) and unemployment (22.5%) or loss in business were more common in male and ill treatment by husband/in-laws (27.5%) in female.

Keywords: Acute; Poisoning; Socio-Economic Pesticide; Suicide.

Introduction

Poison is a substance which has deleterious effect on living organisms produces ill health or death by direct contact or by absorption in the body. With advancement in science and technology large number of harmful chemicals especially insecticides and pesticides are invented to protect farming. But now they become a serious threat to human lives. Acute poisoning forms one of the common causes of emergency hospital admissions. Pattern of poisoning in a region depends on variety of factors, such as availability of the poisons, socio-economic status of the population, religious and cultural influences and availability of drugs. The commonest agents of poisoning in India appear to be pesticides, sedatives, chemicals, alcohol, plant toxins, household poison and snake bite etc. Of late, Aluminium Phosphide has begun to emerge as a major player in the toxicological field, particularly in some northern Indian states. Among the adults, females predominate in all age groups, with an evident preponderance in the second and third decades of life. Acute poisoning in children is almost entirely accidental, while in adults it is mainly suicidal. Mortality and morbidity of poisoning cases varies from country to country depending on the nature of poison and availability of facilities and treatment by qualified doctors.[1] Among children the commonest culprits include kerosene, household chemicals, drugs, pesticides and garden plants [2,3].

Hapur though an agriculture dominant belt of western Utter Pradesh, its geographical proximity to National Capital Region Delhi exposes youths to higher living standards and western culture including consumption of alcohol and other intoxicating drugs. This all forces them sometimes to take hasty decision to end their lives. Poisoning cases can be deliberate or accidental. Poisons are silent weapons, which can be easily used without violence and often without arousing suspicion [4].

Result

A total of 140 cases of poisoning were studied out of which 87 cases were male and 53 female. Highest numbers of cases (62) were from 21-30 year age group, followed by 33 cases from 31-40 years age group. Five cases were below ten years of age and only 9 cases were more than 50 years of age (Table 1).

Most common poison found was Organophosphate (52 cases) followed by Celfos poisoning (30 cases) and 26 cases were of unknown poisoning comprising about two third of the total cases. Two cases of snake bite along with alcohol, dhatura, kerosene and acid poisoning, each below ten cases were found (Table 2).

Of the total 87 male victims, 63 were married and 24 unmarried while in females out of 53, unmarried were 12 and married 41 (Table 3).

Suicidal was the most common manner of poisoning found in 120 cases out of which 76 were male and 44 females. Accidental poisoning was found in 20 cases comprising 11 male and 9 females. No case of homicidal manner was reported (Table 4).

Table 1: Age and Gender wise distribution of Poisoning cases.

Age	Male	Female	Total
00-10	03	02	05
11-20	09	06	15
21-30	41	21	62
31-40	19	14	33
41-50	09	07	16
>50	06	03	09
TOTAL	87	53	140

Table 2: Type of Poisons

Poisons	Cases	Percentage
Organophosphate	52	37.1
Celphos	30	21.4
Unknown	26	18.6
Alcohol	10	07.1
Dhatura	07	05.0
Kerosene	06	04.3
Acid	07	05.0
Snake Bite	02	01.4
Total	140	100

Table 3: Marital status of the victims

Status	Male (%)	Female (%)	Total (%)
Unmarried	24 (27.58%)	12 (22.64%)	36 (25.71%)
Married	63 (72.41%)	41 (77.35%)	104 (74.28%)
Total	87 (100%)	53 (100%)	140 (100%)

Table 4: Manner of poisoning

Manner	Male	Female	Total	%Age
Accidental	11	9	20	14.3
Suicidal	76	44	120	85.7
homicidal	0	0	0	0
total	87	53	140	100

By detailed and thorough history it was found that most common motive behind the suicidal poisoning was family quarrel (31.7%) and ill treatment by the husband or in-laws (27.5%) followed by the unemployment or loss in business (22.5%), while in a very large group (22.5%) the motive was still unknown. In 8.6% cases each, the motive was love affairs and failure in exams (Table 5).

Out of total 140 cases, 63 cases were successfully discharged, 69 cases left against medical advice and 8 (5.7%) cases died during the course of treatment (Table 6).

Most of the cases belonged to middle (60.7%) and lower class (33.6%) while very few cases (5.7%) belonged to high socio economic status (Table 7).

Table 5: Motive behind the Suicidal Poisoning.

Motive	Cases	%Age
Family quarrel	38	31.7
Unemployment/ loss in business	27	22.5
Ill treatment by husband/ in-laws	33	27.5
Failure in exams	12	10
Poverty	01	0.8
Love affairs	12	10
Loneliness	11	9.1
unknown	27	22.5

* Total exceeds 120 cases because more than one motive involved per case

Table 6: In-Hospital status of all the Poisoning cases

In Hospital Status	Number of Cases
Stable	63
Lama	69
Death	08
Total	140

Table 7: Socioeconomic status based distribution of all cases

Socio-Economic Status	Number of Cases (%)
Low	47 (33.6)
Middle	85 (60.7)
High	08 (5.7)
total	140 (100)

Discussion

Many retrospective studies on poisoning pattern were done by various authors of different parts of India. And they observed and emphasized a strong relationship between social parameters and the pattern of poisoning. The present study also highlights the fact that not only the availability of a poison in a region is a sole determinant but also the social parameters play an important role in pattern of poisoning. Gargi et al [5] observed that male to female ratio was nearly 3:1, majority of the victims were in the age group of 21-30 years, and 69.12% were married. Dhanya et al [6] stated that the male: female ration is of 1.27:1 and maximum victims were from the age group 15-30 (58.58%) [3] .

Ali et al [7] also found that majority of the cases was young people from the age group 16-40 years (about 80%). The current study has come up with very similar findings i.e. maximum victims were from the age group of 16-30 years. However, the male: female ratio is 2:1 and in agreement with Dhanya et al. This age range is a period in which a person is most active in all respects be it family life, professional life, or social life, which increases the stress and often leads to devastating outcomes.

Pokhrel et al [8] found that females were more susceptible to the intentional poisoning than male. Intentional poisoning for unmarried male was found to be more (34%) than for female. On the contrary, intentional poisoning in female was high in case of married subjects (57%). The present study also clearly shows vulnerability of poisoning among married subjects is high and that too in married females.

Dhanya et al observed that Organophosphorus (OP) poisoning constitute maximum number of cases (37.25%) followed by unspecified drugs in Calicut. Gupta et al [9] confirmed through chemical analysis report that insecticide was the commonest poison (72.44%) followed by aluminum phosphide (14.28%) and acid (0.63%).

Garg et al [10] reported that Aluminium phosphide is leading cause of poisoning (36.8%) followed by insecticides (31.6%) in South-West Punjab. Gargi et al also reported that Aluminium phosphide (38.23%) followed by Organophosphorus compounds (17.64%) were the commonest poison in Amritsar during 1997-98. However, the present study is in agreement with Dhanya et al and Gupta et al and observed that Organophosphorus poisoning constitute major chunk of total cases (37.1%) in Hapur (UP) region.

It appears that OP poisoning constitutes majority of cases because of easy availability, low cost, unregulated sale and also presence in majority of households in this region.

The present study observes that the contribution of kerosene (4.3%) indicates awareness among parents about the household poisons. However, the childhood poisoning as a result of consuming any unknown substance is still common.

Suicide was the commonest manner of poisoning and many authors made this observation on the basis of history provided by the investigating officers or relatives. Ali et al. in a study on clinical pattern and outcome of OP poisoning showed that suicide is the most common modes of poisoning and reported in 65% cases, followed by accidental (27%) and homicidal (8%).

The current study has also come with a similar pattern in overall poisoning cases i.e. 85.7% suicidal, 14.3% accidental and no homicidal poisoning. Therefore suicide is still the leading cause of poisoning followed by accidental.

Roberts et al [11] mentioned that use of a poison for a purpose is determined by a number of factors including its easy availability in the market, price and popularity among the masses and appropriate laws concerning the poisonous agent. Nigam et al [12] reported that maximum incidence of OP Poisoning is seen in persons engaged with agricultural fields (39.60 %) followed by house wives (20 %) and students (16.85 %).

The current study is in complete agreement with Roberts et al and found that availability, price and laws influence the use of an agent as a poison to a great extent. Dhanya et al. mentioned that general measures like Gastric lavage (83%) and Ryles Tube Aspiration (80%) were mainly used for management of poisoning cases. The current study has come up with very similar findings. Maximum poisoning victims underwent gastric lavage as a general measure. However, remaining 5% cases in which gastric lavage was not at all done include cases of acid ingestion and kerosene. So, Gastric lavage and Ryle's Tube aspiration is still the mainstay of treatment in maximum of cases.

Maiti et al [13] conducted a review study and concluded that use of atropine and oximes derivatives in OP poisoning remains conflicting and controversial. They have no effect in moderate and severe poisoning and do more harm than good. However, Pralidoxime (PAM) is more effective in OP poisoning than atropine. The current study shows that all cases of OP poisoning have been dealt with atropine and PAM and shows good result. So, Atropine and PAM are effective in OP poisoning cases.

Dhanya et al stated that out of the total poisoning cases, 205 patients (10.85%) died of poisoning, of which Organophosphorus poisoning accounted the maximum (88.78% of total mortality). Ali et al graded the Organophosphorus poisoning cases into mild (12%), moderate (60%) and severe (28%) and reported mortality in 20% cases. The present study also showed similar findings. OP poisoning accounted for37.1% of poisonings which is the maximum and 5.7% victims died.

Conclusions

The present study was planned to study the pattern of poisoning in the Hapur district region of Uttar Pradesh, The Male: Female ratio for poisoning in this region was 2:1 and 74.28% of victims were married. Maximum cases of poisoning came from the age group of 21 – 30 years of age and OP poisoning (37.1%) is still the leading cause of poisoning in this region followed by Celphos (21.4%) and unknown poisoning (18.6%).

Suicidal poisoning was responsible for 85.7% of poisoning followed by accidental. Family problems and ill treatment/depression were leading causes of poisoning in this region. Mortality due to poisoning was low with only 5.7% deaths. General measure for management of poisoning was gastric lavage which was done in 95% of cases.

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The Indian Laws Relating to Drugs and Poisons

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Abstract

Drugs are vital means for the prevention and cure of diseases and ailment of different nature. It has played a vital in the health of humanity and improved its life span and quality of life. With the advancement of science and research, new drugs are evolving each year and the pharmaceutical companies are flourishing with business. Therefore various acts have been passed by the Govt. to regulate the manufacture, composition and sale of these drugs. Besides it has made various laws to prevent the misuse of these drugs to harm others. The physicians and the pharmacist should be aware of the various legal acts of drugs and poisons pertaining to its profession. This review article has attempted to bring out all the relevant acts and rules pertaining to drug and poison relevant to the medical practitioners.

Keywords: Drugs; Poisons; Laws; Narcotics; Psychotropic substance.

Introduction

In India several legal acts have been passed to regulate and control the manufacture, sale, distribution, and possession of drugs and poisons. The WHO (1996) definition, drug [7] is any substance or product that is used or intended to be used to modify or explore physiological systems or pathological states for the benefit of the recipient. As per the drug and cosmetic act, drug includes all medicines for internal or external use of human beings or animals and all substances intended to be used for or in the diagnosis, treatment, mitigation or prevention of any disease or disorder in human beings or animals including preparation applied on human body for the purpose of repelling insects like mosquitoes. Poison is defined as any substance which when introduced into the living body or brought into contact with any part thereof will produce ill effect or death by its local or systemic action or both. Some of the Indian laws of importance in relation to drugs and poison are as follows:

- The Poison Act, 1919
- The Drugs Act, 1940
- The Drugs and Cosmetics Act, 1940
- The Drugs and Cosmetics Rules, 1945
- The Pharmacy Act, 1948
- The Drugs Control Act, 1950
- The Drugs and Magic Remedies Act, 1954
- The Narcotics Drugs and Psychotropic Substance Act, 1985
- The Indian Penal Code (IPC),1860
- The Criminal Procedural Code (CrPC),1973
- The Indian Evidence Act (IEA),1872

The Poison Act (1919)

This was amended in the year 1958 and repealed in 1960. It regulates the grant of licenses and sale of poisons whether wholesale or retail. It also regulates import of any specified poisons. It extends to whole of all of India.

The Drugs and Cosmetics Act (1940)

This Act was amended in 1964 to include Ayurveda and Unani drugs and it regulates the drugs of articles of cleansing (except soap), beautifying and promoting attractiveness or altering appearances. It was recently amended in 2008 and today the act is referred to as the Drugs and Cosmetics Amendment Act (2008). This act also demands the fact that every patented or proprietary medicinal preparation under this act must display a label on the container mentioning the exact formula or list of ingredients in it. This act empowers the central Govt. to form a drug technical advisory board and to establish a central drug laboratory to help and advice both the central and states government. It controls the quality, purity and strength of drugs for safety. It regulates the import, manufacture, distribution and sale of these drugs. The amended act has enhanced the scale of punishment for various offences, including sale of spurious drugs, adulteration of drugs and cosmetics, toxic contamination etc.

The Drugs and Cosmetics Rules (1945) [6]

This is a derivative of Drugs and Cosmetic Act 1940; and it covers all kinds of drugs used in therapeutics under allopathic, Ayurvedic, Unani and Siddha preparations. The rule deals mainly with the standard and quality of drugs. It also controls the drugs by specific regulation laid down for their storage, display, sale, dispensing, labeling, prescription etc. To advise the central and state government on technical matters relating to drug control, the following boards have been set up: The drugs and technical advisory board, The ayurvedic and unani technical advisory boards, and the drugs consultative committee. In order to facilitate the analysis or testing of drug samples to assess their quality, the central drugs laboratory was established in 1962. Stringent punishments have laid down for manufacture, stocking, or sale of substandard or spurious drugs. Guidelines for conducting clinical trials for new drugs have been made more strict (Schedule Y). The drugs and cosmetics rules have classified drugs into various schedule as follows.

Schedule C and C1- Biological and special products such as serums, vaccines, etc.

Schedule D – Substances not intended for for medicinal use – condensed or powdered milk, oats, spices and condiments etc.

Schedule E1- Lists of poisonous substances under Ayurvedic, Siddha and Unani systems of Medicine.

Schedule G- List includes hormone preparations, hypoglycaemic agents, antihistamines and anticancer drugs.

Schedule H and L - These are drugs or poisons which need to be labeled as 'Schedule H Drug Warning- to be sold by retail on the prescription of Registered Medical Practitioner only.' Barbiturates, amphetamines, reserpine, ergot, antibiotics, antibacterials and some of the sulphonamides are listed under this schedule.

Schedule J- Drugs,which should not be advertized for certain diseases (which cannot be announced). This covers list of drugs which are claimed to be cure of conditions such as appendicitis, blindness, cancer, cataract, epilepsy, hydrocoele, etc.

Schedule L- Antibiotics, antihistaminic and other chemotherapeutic agent of recent origin subjected to same restrictions as Schedule H drugs.

Schedule O – Standards to be followed with regard to disinfectant fluids.

Schedule X drugs – Barbiturates and certain other sedatives, amphetamines, etc.

The Pharmacy Act (1948)

This Act makes provision for regulation of the profession of pharmacy and for the purpose of constitution of pharmacy council of India, which regulates study of pharmacy throughout the country. Individual states have State Pharmacy Councils for registration of pharmacist. The objective of this act is to allow only registered pharmacists to compound, prepare, mix, or dispense any medicine on the prescription of a registered medical practitioner

The Drugs Control Act (1950)

This Act regulates the supply and distribution of drugs, and also guides the manufacturer or dealer in fixing the maximum price fix every drug.

The Drugs and Magic Remedies (Objectionable Advertisement) Act, 1954

The objective of this act is to ensure that ethical standards are maintained when drugs are advertised by manufacturers. This act bans the objectionable advertisements of magical remedial drugs for curing conditions such as venereal diseases, impotency, menstrual disorders, infertility, abortion, misconception, insanity etc. Advertisements offending decency or morality can be banned under this Act.

The Narcotic Drugs and Psychotropic Substance (NDPS) [2] Act, 1985

This Act consolidates and amends the law relating to narcotic drugs (The Opium Act, 1857 and 1878; and The Dangerous Drug Act, 1930, both are repealed by this Act), drugs of abuse, penalties for the drug trafficking offenses and control over psychotropic substances. Narcotic drugs under this act include opiates, cannabis and cocaine. The psychotropic drugs under this Act refers to mind alerting drugs such as LSD, phencyclidine, amphetamines, barbiturates, methaqualone, benzodiazepines, mescaline, psilocybin and designer drugs (MDMA, DMT, etc). It was again amended in 1988 and 2001. It prevents trafficking in narcotic drugs and psychotropic substances. It is applicable to all citizens of India even though they may be outside the territory of India and to all persons on ships and aircrafts registered in India, wherever they may be. The NDPS act imposes complete prohibition on the cultivation of coca, poppy, and cannabis plants and the manufacture, sale, purchase, use or transport of any narcotics drugs or psychotropic substance except for medical or scientific purposes.

The minimum punishment for any offence committed under the act is 10 years rigorous imprisonment and fine of Rs 1 lakh, while the maximum punishment is 20 years rigorous imprisonment and fine of Rs 20 lakhs. To constitute an offence the first time around, the minimum quantity seized should be equal to or over 250 mg for heroin, 5 gm for hashish or charas, 5gm for opium, 125 mg for cocaine, and 500 gm for ganja.

The central Government of India constituted a Narcotic control Bureau in 1986 with its head quarter at New Delhi, and Zonal offices at Mumbai, Kolkata, Chennai and Varanasi. In 1988, the central government constitute the Narcotic Drugs and psychotropic substance consultative committee, consisting of a chairman and 18 members from various fields who would among other functions, conduct periodic review of the NDPS act. The NDPS act prohibits cultivation of poppy, cannabis, and coca plant. But it allows restricted cultivation of these plants under strict control for scientific and medical use.

Drugs (Price Control) Order, 1995

The Drugs price control order, 1995 was brought in by Govt. of India to regulate and control the manufacture and pricing of the first schedule drugs. It has the power to fix the maximum sale prices of bulk drugs in the first schedule and also the information to be furnished by the manufacturers in relation to the scheduled bulk drugs and non scheduled bulk drugs. It can also fix the retail price of scheduled formulations. The manufacturers should maintain a proper record of drugs and production for inspection.

List of First Scheduled Drugs

The Indian Penal Code (IPC), 1860 [1,3]

- *Section 176:* Doctors must report all cases of homicidal poisoning to police, if not they are punishable
- *Section 177 :* For furnishing false information
- *Section 193 :* Doctor is punishable for giving false information about poisoning case
- *Section 201:* Causing disappearance of evidence of offence
- *Section202:* Doctor is punishable for intentional concealing of facts about poisoning case treated by him.
- *Section 272:* Adulteration of food or drink intended for sale
- *Section 273:* Sale of noxious food or drink
- *Section 274:* Adulteration of drugs
- *Section 275:* Sale of adulterated drugs
- *Section 276:* Sale of drugs as a different drug or preparations
- *Section 284:* Lays down penalty for any person causing harm by rash and negligent handling of a poisonous substance so as to endanger human life or to be likely to cause hurt injury to any person.
- *Section 299:* Culpable homicide including that caused through administration of some poisonous substance.
- *Section 300, 302,306,307,309:* Murder including that caused through administration of poisonous substances with the intention of causing death.

- *Section 304A:* Rash and negligent act including that caused through poisoning
- *Section 320:* Causing grievous hurt
- *Section 324:* Causing hurt by dangerous weapons or means (including Poison or any corrosive substance)
- *Section 326:* Causing grievous hurt by dangerous weapons or means (including poison)
- *Section 326 A:* Voluntarily causing grievous hurt by use of acid(vitriolage)
- *Section 326 B:* Voluntarily throwing or attempting to throw acid.
- *Section 328:* Causing hurt by means of poison or stupefying intoxicating or unwholesome drug or other thing with the intent to commit an offence.

The Code of Criminal Procedure (CrPC), 1973

Section 39: Every person aware of the commission of, or of the intention of any other person to commit any offence punishable under IPC shall forthwith give information to the nearest magistrate or police officer of such commission or intention.

Section 40: Every employed officers aware of the commission of, or of the intention of any other person to commit any offence punishable under IPC shall forthwith give information to the nearest magistrate or police officer of such commission or intention.

Section 175: Power to summon persons by police officer proceeding under section 174

The Indian Evidence Act (IEA), 1872

Section 32, Clause 1, under the Indian Evidence Act (IEA) allows a doctor to record dying declaration when the death of the patient is imminent and arrival of magistrate is delayed.

Recent Amendments of IPC Dealing with Acid Attack Case, 2013 [4,5]

IPC 326 A (Voluntarily Causing Grievous Hurt by Use of Acid, etc.)

Whoever causes permanent or partial damage or deformity to, or burns or maims or disfigures or disables, any part or parts of the body of a person or causes grievous hurt by throwing acid on or by administering acid to that person, or by using any other means with the intention of causing or with the knowledge that he is likely to cause such injury or hurt, shall be punished with imprisonment of either description for a term which shall not be less than ten years but which may extend to imprisonment for life, and with fine: provided that such fine shall be just and reasonable to meet the medical expenses of the treatment of the victim: provided further that any fine imposed under this section shall be paid to the victim. The section was introduced on the basis of the recommendation of justice J.S Verma committee.

IPC 326 B (Voluntarily Throwing or Attempting to Throw Acid)

Whoever throws or attempts to administer acid on any person, or attempts to use any other means, with the intention of causing permanent or partial damage or deformity or burns or maiming or disfiguring or disability or grievous hurt to that person, shall be punished with imprisonment of either description for a term which shall not be less than five years but which may extend to seven years, and shall also be liable to fine.

For the purposes of section 326 A and this section, acid includes any substance which has acidic or corrosive character or burning nature, that is capable of capable of causing bodily injury leading to scars or disfigurement or temporary or permanent disability. For the purposes of section 326 A and this section, permanent or partial damage or deformity shall not be required to be irreversible.

Supreme court in Laxmi Vs Union of India directed the state to consider (1) Enactment of appropriate provisions for effective regulation of sale of acid in the sates/Union territories (2) Measures for proper treatment, after care and rehabilitation of the victims of acid attack and needs of acid attack victims (3) Compensation payable to acid victims by the state/ or creation of some separate fund for payment of compensation to acid attack victims. In a subsequent order in the same case the supreme court issued many directions to curb the menace of acid attacks.

Supreme Court Guidelines to Prevent Acid Attacks

1. Over the counter, sale of acid is completely prohibited unless the seller maintains a log/ register recording the sale of acid which will contain the details of the person(s) to whom acid(s) is/are sold and the quantity sold. The log/register shall contain the address of the person to whom it is sold.
2. All sellers shall acid only after the buyer has

shown:

a. A photo ID issued by the government which also has the address of the person.

b. Specifies the reason/purpose for procuring acid.

3. All stocks of acid must be declared by the seller with the concerned Sub Divisional Magistrate (SDM) within 15 days
4. No acid shall be sold to any person who is below 18 years of age.
5. In case of undeclared stock of acid, it will be open to the concerned SDM to confiscate the stock and suitably impose fine on such seller upto 50,000-
6. The concerned SDM may impose fine upto 50,000/- on any person who commits breach of any of the above directions.

The educational institutions, research laboratories, hospitals, Government departments and the departments of public sector undertakings, who are required to keep and store acid, shall follow the following guidelines:

1. A register of usage of acid shall be maintained and the same shall be filed with the concerned SDM.
2. A person shall be made accountable for possession and safe keeping of acid in their premises.
3. The acid shall be stored under the supervision of this person and there shall be compulsory checking of the students/personnel leaving the laboratories/place of storage where acid is used.

Conclusion

In India we have various acts and laws to regulate drugs and poisons. It is important to know its legal aspects when we prescribe and dispense these drugs in hospital or pharmacy. Its awareness can help us to avoid negligence due to our ignorance of these rules and also provide prudent medico-legal opinion related to drug and poison.

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Review Article

Developments in Analysis of Fire Debris Residues

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Abstract

This review gives a brief overview of the recent developments in the field of analysis of petroleum products in fire debris residues by different spectroscopic and chromatographic techniques for forensic purpose. The review covers different aspects of analysis such as the types of accelerants, substrates involved, isolation procedures, column and mobile phase used, and subsequent detection in tabular form. This paper covers detection of petroleum products such as petrol, kerosene and diesel in various types of samples recovered in arson cases.

Keywords: Fire Debris Residues; Inflammable Liquids; Petroleum Products; Solid Phase Microextraction; Gas Chromatography-Mass Spectrometry.

Introduction

Any chemical substance used to initiate or increase the intensity or speed of spread of fire is known as fuel. It is used to intentionally start or spread fire. Not all inflammable liquids found at a fire scene are accelerants and conversely, not all accelerants used to commit arson are liquids [1,2].

Accelerant may be a solid, liquid or in some cases gas. Liquid fire accelerants include highly inflammable and volatile liquids petroleum products, solvents etc. Petroleum products such as petrol, kerosene and diesel are more frequently used than other inflammable liquids such as alcohols, paints, lacquer thinners, ether and industrial solvents [1].

Arson is one of the most difficult crimes to investigate because of its destructive nature. The crime itself destroys the physical evidence at its origin. Most of the evidences are destroy in burning process and rest are destroy during fire extinguish process. Arson is the one crime that destroys, rather than creates evidence as it progresses [3].

Flammable liquids are not frequently present in case of unintentional fires and unexplained presence of these liquids thus strongly indicates a fire of suspicious origin. Detection and identification of these accelerants are therefore helpful in determining origin and cause of fire [4].

The crime of arson falls under the Indian Penal Code (1860) section 435, 436 and 438. Arson is considered as violent crime affecting the public safety and peace [5].

Petroleum products (petrol, kerosene and diesel) are frequently used to commit arson due to their easy availability, simple handling, storage and cost effectiveness. Petrol is highly inflammable and volatile substance. Kerosene is less volatile than petrol. It is available as a subsidized domestic cooking fuel and is often misused as a fire accelerant in arson and bride burning cases [1].

Detection of these accelerants is thus of vital importance. Partially burnt exhibits including clothes, carpet, wood, soil, hairs, paper, concrete recovered from body of victim, accused and crime scene may be referred to forensic science laboratories for the detection and characterisation of petroleum residues. Sample should be store with utmost care and its loss and contamination should be avoided during transfer to laboratory and following analysis as it affect the outcome of analysis and also raise the question about the integrity of sample in court. Standard sampling procedure should be followed with the proper documentation in order to uphold sample integrity and chain of custody [3,6].

Different kinds of containers can be used for this purpose. Sample containers may vary from bags to jars and metal cans and each of them have their own merits and demerits. Containers used to store the fire debris sample should be clean, inert, and durable and does not itself provide a source of cross-contamination. It is observed that many types of plastic bag contain interfering compounds [6].

Tontarski Jr. advocate that polyethylene containers should be avoided to collect the fire debris samples due to significant accelerant loss and sample contamination. Therefore, containers of unknown quality should be avoided and only ''certified containers'' should be used [7].

Fire debris may contain trace amounts of inflammable substances. Many classical physical and chemical methods are used for the detection and identification of accelerants in fire debris residues. But these methods are time-consuming, less sensitive and not reliable. Therefore, sophisticated instrumental analytical techniques are frequently used to analyse trace amounts of accelerants in fire debris residues.

Thus on the basis of frequent use of petroleum products in arson cases, it seems to be necessary to summarize recent spectroscopic and chromatographic procedures used to identify them in fire debris residues samples. So, we select the detection of petrol, kerosene and diesel in various complex matrices of forensic interest by different conventional and modern instrumental techniques. The aim of this compilation is to give an overview on analysis of petroleum products (including extraction procedure, separation and identification by different techniques) in different kinds of matrices. Table 1 reflects the characteristics of different GC and GC-MS methods for analysis of accelerants in fire debris samples.

Analysis of Petroleum Products

Development of analytical methods that are capable of detecting trace amounts of petroleum products in fire debris samples has become increasingly important in the field of forensic science. Routine analyses rely on the visual comparison of chromatogram of sample with chromatogram of standard petroleum product. Most of reviews provide information regarding the different sample preparation methods used for the analysis of the accelerants in fire debris residues [8-10].

There is a need for a review providing recent information on their analysis in different arson debris samples. Therefore, we compile different analytical methods (including extraction) used for analysis of petroleum products in fire debris samples. Petroleum products such as petrol, kerosene and diesel are frequently encountered in arson cases and in cases of suicidal or homicidal burning associated with bride burning in dowry disputes. These accelerants are present in traces in partially burnt exhibits such as mattress, wood, plastic, paper, carpet, clothes etc. Techniques used for isolation and concentration of accelerants from different substrates have changed from time to time. In 1950's and 1960's, steam distillation, vacuum distillation and solvent extraction procedures were used to extract accelerants from substrates and are considered as conventional extraction procedures [11,12].

In early 1970's, headspace extraction procedures were introduced in fire debris analysis and are considered as modern extraction procedures [6,11].

These headspace extraction procedures include direct (heated) headspace analysis, static headspace analysis such as carbon strip method, solid phase micro-extraction (SPME) and dynamic headspace analysis (purge and trap analysis). Various screening methods and instrumental techniques can be used for the extraction and detection of accelerant residues. These methods are discussed as follows:

Spectroscopic Methods

Spectroscopic methods are based on measurement of signal generated by the interaction of electromagnetic radiations with matter. These methods provide both qualitative and quantitative information about the analyte. However, due to the impurities and complex nature of petroleum products and matrices received in arson cases, these methods are not frequently used to establish the identity of analyte. These methods can be used as a screening method at the initial stage of analysis.

Adams described the different procedures (I. and II.) used for the extraction of small amounts of accelerants from arson debris depending on boiling product (low or high). In procedure I., air was pumped through the system at rate of about 1l/min for 2 to 3 mins. Sample was collected in jar and concentrated by heating with a 300W reflector flood bulb. Sample may be recovered as a mixture of solid and liquid. Procedure II. involves the washing of debris with carbon tetrachloride. These washings were collected, combined and concentrated by evaporation at room temperature. Infrared spectroscopy was used to pinpoint the identity of accelerants. He concluded that these procedures were efficient and rapid for the extraction of minute quantities of accelerants from arson debris [13].

Bryce et al. analysed fire debris samples using nuclear magnetic resonance spectroscopy. Samples were subjected to steam distillation in order to extract accelerants from samples and an aliquot amount of distillate was placed in 2ml sample vials. Tetramethylsilane was used as an internal standard. Deuterated chloroform was used as a solvent. They observed that technique is independent of interfering substrate due to its low sensitivity. They also observed that different solvents have no significant effect on spectrum. As little as 0.25ml of sample is sufficient for analysis. They concluded that nuclear magnetic resonance spectroscopy complements the present analytical techniques and could provide a powerful tool for use in fire debris analysis [14].

Meal analysed the fire debris samples by using second derivative ultraviolet spectroscopy. Samples were extracted with cyclohexane and extracts were scanned in the range of 245-320nm. Quartz cells of 1cm path length were used. He observed a unique and easily recognizable second derivative UV spectrum of different accelerants including thinners and spirits and concluded that second derivative ultraviolet spectroscopic method is rapid, sensitive, simple and cost effective for analysis of fire debris and independent of matrix interference [15].

Mc Curdy et al. developed a method for the analysis of arson accelerants in fire debris by using vapour phase ultraviolet spectroscopy. They compared the present method with conventional GC-FID and GC-MS method and found that vapour phase ultraviolet spectroscopy is rapid, inexpensive and sufficiently sensitive to be of use for the analysis of arson accelerants. 10cm path length quartz cell was used. Spectra were recorded over the wavelength range 230-280nm. 1µl of sample is sufficient to record vapour phase UV spectra. They concluded that method could be used as alternative to currently existing techniques for analysis of arson accelerants [16].

Liu et al. developed a portable and cost effective cataluminescence based vapour sensitive sensor array for rapid detection and discrimination of flammable liquid vapours. They used linear discriminant analysis and hierarchical cluster analysis to discriminate fingerprints of flammable liquid vapours. Photomultiplier tubes were used to detect the cataluminescence signals. Heating voltage for sensor array was maintained at 5.5V. They observed that water vapours did not cause significant interference in detection process. They also observed that different analytes could be 'fingerprinted' by their unique patterns of cataluminescence intensities. They noted that sensor array reduces the interference caused by complex combustion background. They concluded that method is useful to discriminate flammable liquid vapours of forensic interest [17].

Chromatographic Methods

Chromatographic methods are used to separate the components of complex mixture. These methods are widely used due to their simplicity, rapidity, sensitivity and cost-effectiveness. These methods cannot provide the definite identity of analyte due to their non-specificity. But coupling of these methods with appropriate spectroscopic method not only enhances the sensitivity but also the selectivity of technique.

Thin Layer Chromatography/High Performance Thin Layer Chromatography (TLC/HPTLC) Methods

Baggi et al. presented a simple and effective thin layer chromatographic method for the detection and characterization of petroleum residues extracted from different substrates such as cloth, paper, wood and leather. 100ml of distillate was collected and extracted with benzene. The benzene fractions were collected, combined and evaporated to dryness at room temperature. n-heptane saturated with 3% v/v formaldehyde was used as mobile phase in TLC. Concentrated sulfuric acid or anisaldehyde was used as chromogenic reagent. Thin layer chromatographic plates coated with silica gel G impregnated with 2% w/w sodium carbonate and silica gel GF 254 were used. They observed that as little as 0.02ml of petroleum residue could be detected and characterized by this method. They also observed that sodium carbonate impregnated plates were more effective than other plates in separation of components of analytes [18].

Dhole et al. developed a method for the detection of petroleum accelerant residues on partially burnt objects in arson or bride burning cases. The method involves the conversion of aromatic hydrocarbons such as naphthalene and alkyl naphthalenes into corresponding phenols or naphthols which were further detected by thin layer chromatography or high performance thin layer chromatography after spraying with diazotized p-nitroaniline reagent followed by aqueous ethanolic sodium hydroxide solution. A mixture of chloroform : xylene (3:1) was used as a solvent system. They observed that petroleum products could be easily differentiated with respect to total number of spots, their colour, position, shape and relative distribution and concluded that although the present method is time consuming and laborious yet it is more sensitive and selective than conventional thin layer chromatographic methods [19].

Malve et al. analysed the dye component of different fake and adulterated petrol samples (genuine petrol, fake petrol, adulterated green petrol) by employing high performance thin layer chromatography. The samples were evaporated on water bath (60-70^{0}C) and residue was dissolve in 0.2ml of benzene. 20µl of sample was spotted on plate and a mixture of hexane: ethyl acetate (19.5:0.5) was used as solvent system. They also studied distillation characteristics of these samples and observed that fake and genuine samples have different temperatures at 90% recovery points. They concluded that distillation characteristics along with dye analysis can be used to confirm the purity and adulteration of petrol samples [20].

Gas Chromatography-Flame Ionization Detection (GC-FID) Methods

Gas chromatography was first applied to fire debris analysis in 1960 [21]. Prior to that, ignitable liquid residues were analysed by different techniques [13,22-25].

Flame ionization detector (FID) is most popular detector used with GC and it is considered as a universal detector for GC. Number of organic samples can be analysed by FID and most GC analyses are performed using FID. Its response is not influence by change in the flow rate of mobile phase and it work as a standard detector for the analysis of hydrocarbons from last three decades due to its high sensitivity, low noise and large linear response range [26].

Lloyd analysed petroleum products of high relative molecular mass by capillary gas chromatography and observed that paraffin wax was mostly resolved while other samples form the characteristic unresolved envelope. He concluded that present method can be used to distinguish different types of petroleum products of high relative molecular mass and visual inspection of chromatograms are sufficient to made such discrimination [27].

Twibell et al. compared the different methods used for the extraction of accelerants from fire debris. They observed that capillary columns offers higher sensitivity than packed columns due to their greater resolution. They concluded that adsorption wire procedure is most sensitive while hot headspace method is least sensitive whereas steam distillation has intermediate sensitivity [28].

Nowicki and Strock compared different extraction techniques used for analysis of fire debris samples. They also optimized the different parameters of extraction procedures. Peak area of 1,2,4-trimethylbenzene was selected to study the efficiency of extraction method. They observed that efficiency of headspace method can be optimized by heating 10ml of sample at 120^{0}C for 20mins. They concluded that charcoal adsorption/elution technique is more efficient than headspace and solvent extraction [29].

Frenkel et al. compared the headspace and adsorption tube extraction technique for the analysis of arson residues. They also compared the two desorption methods (thermal desorption such as pyrolysis and solvent extraction) used with adsorption tube technique. They also studied the effect of water on analysis of arson residues. They suggested that Zeolite 4A (0.4nm pores, 2g/1ml of water) molecular sieves could be used to eliminate the interference caused by water. They observed that solvent extraction method was as sensitive as thermal desorption (such as pyrolysis) but cracking was observed in later. They concluded that adsorption tube method is more sensitive, efficient and useful than headspace method [30].

Reeve et al. compared charcoal adsorption and direct headspace injection techniques to isolate accelerants from fire debris and concluded that direct headspace injection technique is simple, sensitive and require minimum sample preparation [31].

Mann compared and discriminate different gasoline samples (neat and evaporated) on the basis of the relative peak intensities. He suggested that boiling point range, relative concentration of major versus minor components, aliphatic and aromatic hydrocarbon content and presence of additives are useful parameters to distinguish different classes of ignitable liquids. He concluded that present comparison method cannot be used to formulate positive conclusion while it is an ideal method to formulate negative conclusion and used for screening of samples at initial stage of investigation [32].

Waters and Palmer advocated the utility of passive headspace concentration technique in multiple analysis of fire debris and concluded that present concentration technique is non destructive, fast and less susceptible to contamination [33].

Almirall et al. developed a method for the extraction and identification of accelerants from aqueous samples of fire debris by using SPME-GC-FID. They also compared this method with solvent extraction procedure using hexane as an extracting phase. They observed the higher sensitivity of SPME as compared to solvent extraction procedure for light petroleum distillate and gasoline while solvent extraction of diesel did not produce identifiable chromatograms. They concluded that SPME technique is more sensitive, less laborious, rapid, solventless technique for the extraction of ignitable liquid from aqueous samples than conventional solvent extraction method [34].

Furton et al. developed a novel method for the analysis of gasoline from fire debris by using SPME. They also compared this method with passive adsorption elution method and concluded that SPME technique is faster, cost-effective, efficient, simpler and sensitive than conventional passive adsorption elution method and it provides reproducible multiple analyses without the need of any organic solvent [35].

Newman et al. studied the effects of different parameters such as adsorption time, adsorption temperature, strip size and concentration of sample on the adsorption of accelerants. They observed that diesel and kerosene products were difficult to discriminate at temperature less than 60^0C.

However, higher temperature (>90^0C) was not recommended due to pyrolysis and decomposition of substrates. 8mm × 8mm strip size and heating at 50-70^0C for 16-24hrs is recommended to produce efficient results. They observed that amount of displacement of lighter components in sample rises with increase in temperature, time, concentration and size of strip [36].

Almirall et al. developed a method for detection and identification of flammable liquid residues on human hand by using SPME-GC-FID. Accelerant was deposited on the hand of a subject and it was then covered with a nylon bag. PDMS coated SPME fibre was inserted into bag and it was exposed to headspace over the hand for 15 mins. Fibre was then inserted into the injection port of gas chromatograph. They concluded that present method is sensitive, simple, inexpensive, fast to detect and identify flammable liquid residue from human skin and can be used in conjunction with an accelerant detection canine team at crime scene [37].

Coulson et al. studied the effect of compressed air foam on detection of hydrocarbon fuels in fire debris samples and concluded that air foam did not cause significant interferences in detection and identification of hydrocarbon fuels [38].

Bodle and Hardy developed a SPME based method for the analysis of petroleum based accelerants. SIMCA and PCA techniques were used to identify and classify the accelerants. The accuracy of classification by SIMCA models for previous and current ASTM system was 98.5% and 97.2% respectively. They concluded that SIMCA is an effective class predictor of accelerants [39].

Darrer et al. compared the efficiency of different mediums (PVC, PE and Latex gloves, humidified filter paper) to collect gasoline from hands. They also evaluated the persistency of petrol on hands using PVC gloves. They observed the massive evaporation of gasoline within 30mins of its deposition on hands and concluded that PVC gloves are effective and efficient medium for collection of gasoline from hands due to low background noise or reduced amount of volatile compounds detected from it [40].

Sanagi et al. developed a method for the analysis of accelerants in fire debris samples by using headspace single drop microextraction (HS-SDME). 10ml of sample solution was placed in 15ml headspace vial and continuously stirred. 2.5µl of benzyl alcohol was withdrawn into a microsyringe and this microsyringe was then inserted into headspace and suspended over sample solution. Benzyl alcohol was then suspended on the tip of syringe needle and drop was withdrawn into syringe after 20 mins of extraction. Then extract was directly injected into injection port of GC. They observed no interferences due to burnt matrix. They concluded that HS-SDME-GC-FID is a rapid, sensitive and simple method and can be used as an excellent alternative method for the analysis of accelerants in fire debris samples [41].

Gas Chromatography-Photo Ionization Detection (GC-PID) Method

This detector measures the current generating from photoionization of analyte by ultraviolet radiation at a suitable electrode. Its high sensitivity for aromatic hydrocarbons, higher selectivity and large linear response range enhances its utility in analysis of complex hydrocarbon mixtures. Thus the combination of FID and photoionization detection for the analysis of complex samples is more useful and advantageous [26].

Higgins et al. compared the extraction efficiencies of two heating techniques, i.e.; convection heating and microwave oven heating. Samples were placed in a polyester bag and metal paint can for microwave oven and convection heating respectively. Accelerants were isolated from carpet material by convection as well as microwave oven heating procedures and these isolated accelerant vapours were adsorbed on activated charcoal sample tube which were further washed with 2ml of carbon disulfide in order to extract accelerants. 1μl of extract was injected into the injection port of GC. Photoionization detector was used due to its high sensitivity. They observed that microwave oven heating procedure is more efficient and heat the samples faster than convection heating. They concluded that conventional convection oven can be replaced with microwave oven for sample heating in order to reduce analysis time and to enhance the sensitivity of accelerant vapour collection [42].

Gas Chromatography-Mass Spectrometry (GC-MS) Methods

Gas chromatography-mass spectrometry is an extremely versatile instrumental technique for the analysis of wide range of volatile compounds. In GC-MS, a gas chromatograph (GC) is attached to a mass spectrometer (MS) via a suitable interface. GC-MS is a hyphenated technique in which two techniques based on completely different principles are coupled together. In GC-MS, GC separates the components of sample while MS identify them. Compounds are separated on the basis of their relative affinity with stationary phase of column. Components eluting from the chromatographic column are then introduced to the mass spectrometer via a specialized interface. Coupling of MS with GC not only detects the analytes but also provide the pinpoint identification of analytes. Therefore MS provides a powerful detection tool in combination with GC [26].

Smith analysed arson debris and standard accelerants (neat and evaporated) by GC-MS used in extracted ion profile mode, i.e., mass chromatography. He observed that mass chromatography can eliminate the interference caused by combustion and pyrolysis products of matrices. Method provides the rapid detection of specific compounds even in the presence of intense background interferences and concluded that mass chromatography is a valuable tool for examining arson debris samples [43].

Tranthim-Fryer described a simple, sensitive and cost effective carbon wire adsorption/solvent extraction technique for the analysis of accelerants and volatile organic compounds in arson debris. He observed that water vapors did not cause any interference in detection and identification of accelerants and concluded that present method allows further examination of samples at later date (if required) and can be suited to those laboratories without a thermal desorption unit or pyrolyzer [44].

Keto and Wineman identified petroleum based accelerants in fire debris by GC-MS. Target compound chromatograms (TCC) of samples were compared with TCC's of their corresponding standards to establish the identity of sample. They observed that target compound patterns for fresh and weathered gasoline, medium petroleum distillates and heavy petroleum distillates were specific and could be used for their identification in high background arson debris samples. They also observed that pyrolysis products have different TCC's from petroleum products. They concluded that target compound analysis is a simple, easy and useful approach for the identification of residual petroleum products in fire debris [45].

Coulombe analysed fire debris samples and different products (low volatility residue from gasoline, evaporated diesel fuel, evaporated gasoline from Molotov cocktail and creosote) by GC-MS and concluded that diphenyldisulfides and its homologues could be considered as chemical markers of weathered gasoline since these components were not present in creosote and other petroleum derivatives. However, there absence cannot eliminate the presence of gasoline [46].

Frontela et al. compared two extraction procedures used to extract accelerants from arson debris by GC-MS in specific mass ion mode and concluded that although adsorption/elution method is faster than distillation but later has higher degree of efficiency [47].

Steffen and Pawliszyn developed SPME method for the detection of liquid accelerants from arson suspected fire debris by using GC-FID and GC-Ion Trap MS. They observed that interferences from arson samples or fire debris could be distinguished from trace amounts of accelerants by using GC-

Table 1: Characteristics of the GC methods for analysis of accelerants in fire debris samples

S. No.	Analyte/s	Matrix	Extraction Technique/s	Column (Dimensions)	Carrier gas (flow rate)	Detector	Injector & Detector Temp.	m/z range	References
1	Petrol, kerosene, diesel	NR	Dynamic adsorption/ elution	DB-1 (30m × 0.25mm × 0.25µm) BP-5 (32m × 0.32mm × 0.5µm)	N_2 (1ml/min) He (1ml/min)	FID, MS	265^{0}C, 280^{0}C	45-500	[16]
2	Paraffin wax, liquid paraffin, gear oil, light oil, lubricating oil, engine oil	NR	NR	OV-1 glass capillary (50m × 0.25mm)	H_2 (4ml/min)	FID	280^{0}C	NA	[27]
3	Petrol, kerosene, diesel	Hardwood charcoal	Hot headspace, steam distillation, adsorption wire technique	OV 1 (25m) 15% Carbowax 20M on chromosorb W packed column (3m × 6.35mm)	N_2 (10psi=inlet pressure) N_2 (60ml/min)	FID	NR	NA	[28]
4	Petrol	Carpet padding	Solvent extraction, steam distillation, direct headspace, sorbent trap/thermal desorption	Supelcoport stainless steel (12′ × 1/8′′)	N_2 (20ml/min)	FID	230^{0}C, 230^{0}C	NA	[29]
5	Petrol, kerosene, diesel	Filter paper	Headspace, Dynamic adsorption/elution	OV-101 Stainless steel (6m × 3.175mm)	NR	FID	NR	NA	[30]
6	Petrol, kerosene, diesel	Paper	Headspace, Passive adsorption/ elution	DB-5 (30m × 0.32mm × 1µm)	H_2 (70cm/sec)	FID	250^{0}C	NA	[31]
7	Petrol, MPD, HPD	NR	Passive adsorption/ elution	SPB-1 (30m × 0.32mm × 0.25µm)	He (2ml/min)	FID	250^{0}C, 290^{0}C	NA	[33]
8	Petrol, diesel, lighter fluid	Water	Solvent extraction, SPME	HP-1 (30m × 0.2mm × 0.25µm)	He (1ml/min)	FID	220^{0}C, 300^{0}C	NA	[34]

9	Petrol	Burned pine, wood, plastic	SPME, Passive adsorption/ elution	HP-1 (30m × 0.25mm × 0.25μm)	1ml/min	FID	220^{0}C, 300^{0}C	NA	[35]
10	Petrol, kerosene, diesel	Wood, kimwipes	Passive adsorption/ elution	DB-1 (12m × 0.25mm × 0.25μm)	He (25.6cm/ sec)	FID	275^{0}C, 280^{0}C	NA	[36]
11	Petrol, diesel, charcoal lighter fluid	Human hand	SPME	DB-5MS (30m × 0.25mm × 0.25μm)	He (1ml/min)	FID	250^{0}C, 310^{0}C	NA	[37]
12	Petrol, kerosene, diesel, white and methylated spirits, mineral turpentine, isopropanol	Tissue paper, soil, unburnt carpet and wood, burnt carpet and wood	Passive adsorption/ elution	DB-1 (25m) Carbowax (30m)	H_2 (30ml/min)	FID	For DCM extracts (260^{0}C, 260^{0}C) For water extracts (150^{0}C, 150^{0}C)	NA	[38]
13	130 accelerants including petrol, kerosene, diesel	NR	SPME	PETROCOL DH 50.2 (50m × 0.2mm × 0.5μm)	N_2 (1ml/min)	FID	270^{0}C	NA	[39]
14	Petrol	Human hand	Passive adsorption/ elution	DB-5 (30m × 0.32mm × 1.0μm)	He (2ml/min)	FID	250^{0}C, 280^{0}C	NA	[40]
15	Petrol, diesel, kerosene	Fabric curtain	Headspace single drop microextraction	Ultra-1 (25m × 0.20mm × 0.1μm)	He (1.5ml/min)	FID	NR	NA	[41]
16	Petrol, dodecane	Carpet	Passive adsorption/ elution	Stainless steel (3.65m × 3.18mm)	N_2 (30ml/min)	FID	NR	NA	[42]
17	Petrol, kerosene, diesel	Tissue paper	Passive adsorption/ elution	BP-1 (25m × 0.25mm × 0.25μm)	He (Head pressure= 120kPa and 35kPa)	FID, MS	NR	NR	[44]
18	Petrol, MPD, HPD	Wood, tile, carpet	Passive adsorption/ elution	DB-1 (60m × 0.32mm × 0.25μm)	He (2ml/min)	MS	260^{0}C	50-200	[45]

19	Petrol	NR	Steam distillation, Passive adsorption/ elution	HP-1 (25m × 0.2mm × 0.33µm)	He (0.5-1ml/min)	MS	250^{0}C	40-500	[47]
20	Petrol, barbecue lighter fluid	Wood, carpet	SPME	DB-5 (30m × 0.25mm × 0.25µm)	NR	FID, MS	275^{0}C, 300^{0}C	50-260	[48]
21	Petrol, diesel	Filter paper	Passive adsorption/ elution	HP-1 (25m × 0.2mm × 0.5µm)	He (100kPa)	MS	NR	33-300	[49]
22	Petrol	Cloth, paper towel	Passive adsorption/ elution	Rtx-1 (30m × 0.25mm × 0.25µm)	0.68ml/min	MS	NR	10-400	[50]
23	51 accelerants including Petrol, kerosene, diesel	Wood, carpet	Passive adsorption/ elution	Supleco (25m × 0.2mm × 0.5µm)	He (40ml/min)	MS	NR	NR	[51]
24	Diesel	Wood, chipboard, plastic, carpet	Passive adsorption/ thermal desorption	Elite-1 (30m × 0.25mm × 1.0µm)	He	MS	NR	NR	[52]
25	Petrol	Car carpet	Passive adsorption/ elution	DB-5MS (30m × 0.25mm × 0.25µm)	He (1.7ml/min)	MS	250^{0}C	40-200	[53]
26	Petrol, lubricant, fuel oils	Water	Passive adsorption/ elution	Elite (1.30m)	NR	MS	NR	35-350	[54]
27	Petrol	Wood, paper, carpet	SPME	HP-5MS (30m × 0.25mm × 0.25µm)	He (1ml/min)	MS	280^{0}C	40-400	[56]
28	Petrol	NR	SPE	HP-5MS (30m × 0.25mm × 0.25µm)	He (1.2ml/min)	MS	280^{0}C	30-350	[57]

29	Petrol, diesel	Carpet (nylon, polyester, wool), wallpaper, synthetic floor	Passive adsorption/ elution	SBP-5 (30m × 0.25mm × 0.25µm)	He (1ml/min)	MS	275^{0}C	37-400	[58]
30	Petrol	Wood	Passive adsorption/ elution	DB-1 (60m × 0.25mm × 1.0µm)	He	MS	NR	29-200	[59]
31	Petrol	Car carpet	Passive adsorption/ elution	HP-5MS (30m × 0.25mm × 0.25µm)	He (1.2ml/min)	MS	280^{0}C	30-350	[60]
32	Petrol, kerosene, diesel, extraction solvent, universal diluter	Carpet, wood, unpainted chipboard	Passive adsorption/ thermal desorption	Elite-1 (30m × 0.25mm × 1.0µm)	He	MS	NR	NR	[61]
33	Petrol, diesel, C$_1$-C$_4$ alcohols, acetone	Filter paper	Passive adsorption/ thermal desorption	Elite-1 (30m × 0.25mm × 1.0µm)	He	MS	NR	NR	[62]
34	Petrol, diesel, mineral spirits, paint thinner, paint remover, lighter fuel, turpentine	Carpets	SPME	Rtx-5MS (30m × 0.25mm × 0.25µm)	He (2ml/min)	MS	270^{0}C	45-200	[63]
35	Petrol	Human hand	Passive adsorption/ elution	HP-5MS (30m × 0.25mm × 0.25µm)	He (1ml/min)	MS	250^{0}C	10-450	[64]
36	Gasoline, diesel	NR	NR	HP-1 (25m×0.20mm×0 .50µm)	He (1ml/min)	MS	280^{0}C	NR	[65]
37	Petrol, kerosene	Carpet, wood	Passive adsorption/ elution	DB-5MS (30m × 0.25mm × 0.25µm)	He (1ml/min)	MS	250^{0}C	50-550	[66]
38	Petrol, diesel, barbecue lighter, turpentine, industrial solvents	Soil, sawdust	HSSE, SPME	VF-23MS (30m × 0.25mm × 0.25µm)	He (1ml/min)	MS	NR	40-400	[67]

39	Petrol, diesel	Human hand	Passive adsorption/ elution	AT-1 (30m × 0.25mm × 0.25µm)	He (3.2ml/min)	MS	NR	30-300	[68]
40	Petroleum distillates (gasoline, kerosene, charcoal lighter fluid, paint thinners)	Carpet, paper, wood, plastic, cloth	Dynamic adsorption/ elution	DB-5 (30m×0.25mm×1 µm) DB-225 (30m×0.25mm×0 .25µm)	H_2 (1ml/min)	FID	280^0C, 280^0C	NA	[71]
41	Petrol, kerosene, diesel, white spirit, charcoal lighter fluid, paint thinners	Wood, carpet, plastic, clothes, painted surface	Dynamic adsorption/ elution	DB-5 (30m × 0.25mm × 1µm)	He (0.9ml/min)	MS	250^0C	50-200	[73]
42	Petrol, diesel, kerosene	Soil, wood, paper	SPME	HP-5MS (30m × 0.25mm × 0.25µm)	He (1ml/min)	MS	280^0C	35-650	[74]

ITMS in ion selective mode. They concluded that HS-SPME is very sensitive, simple and rapid technique for the extraction of small amounts of accelerants from fire debris [48].

Lentini and Armstrong compared the eluting efficiencies of carbon disulfide and diethyl ether and suggested that carbon disulfide is best solvent to elute compounds of interest from adsorption packages prior to analysis GC-FID but when GC-MS is used, diethyl ether is better choice of solvent than carbon disulfide because its eluting efficiency is comparable to carbon disulfide and it poses a much smaller health risk to fire debris laboratory personnel [49].

Gilbert described the potential use of extracted ion profiles in distinguishing an ignitable liquid from interference due to pyrolysis or other contaminants and concluded that individual extracted ion profiles are better than summed extracted ion profiles in identifying ignitable liquids [50].

Tan et al. identify and classify petroleum based accelerants using GC-MS and multivariate pattern recognition techniques such as Principal Component Analysis (PCA) and Soft Independent Model Classification Analogy (SIMCA). Detection limits of correct classification depends on sample class and were in the range of 5-50µl. They suggested that carpet is better source than wood for collection of accelerant residues. They concluded that PCA and SIMCA can be successfully applied to classify accelerants after GC-MS analysis [51].

Borusiewicz studied the effect of fire extinguishers such as foam, powder and snow extinguisher on detection and identification of diesel in arson debris and suggested that fire fighting action of fire extinguishers should be rapid as this factor plays a significant role in recovery of accelerants from fire debris samples. They concluded that these fire extinguishers did not cause any interference in isolation, detection and identification of accelerants from fire debris samples [52].

Cavanagh et al. studied the background interferences generated from car carpets. They also investigated the persistency of petrol on carpet. They observed that deposition of target compounds onto carpet depends on occupation and behaviour of occupants and suggested that presence of larger volumes of petrol on carpet is an indicative of intentional addition of petrol to vehicle interior. They concluded that car carpets exhibit some of the compounds that may interfere with the detection and identification of petrol residues [53].

Zadora et al. identify petroleum products in arson debris and water by GC-MS and concluded that present method is rapid, sensitive and useful for analysis of samples even after several months of their collection [54].

Doble et al. classify premium and regular gasolines using PCA. They compared PCA and ANN's for classification of premium and regular gasolines from their GC-MS chromatograms. They concluded that PCA is a potential statistical tool to classify gasoline samples into either premium or regular class while ANN's are reliable and accurate statistical tool to classify gasolines into premium or regular groups and into seasonal formulation based subgroups [55].

Lloyd and Edmiston investigated the extraction efficiency of SPME fibers (PDMS and Carboxen/PDMS) used for extraction of hydrocarbons from fire debris samples and concluded that Carboxen/PDMS fibers are more efficient for the extraction of aromatic hydrocarbons compared to aliphatic hydrocarbons [56].

Sandercock and Du Pasquier identify and differentiate 35 gasoline samples using GC-MS after extracting trace polar and polycyclic aromatic hydrocarbon compounds using solid phase extraction. Linear discriminant analysis divides 35 samples into 32 unique groups. They concluded that polycyclic aromatic hydrocarbons can be used to distinguish between different gasoline samples due to their significant variation from sample to sample [57].

Almirall and Furton characterize the background and pyrolysis products that were generated during control burning of different substrates. They observed that many substrate backgrounds, combustion or pyrolysis products were also target compounds of ignitable liquid residue mixtures and could interfere with identification process. They suggested that negative control samples of substrates present at fire scenes should be collected and analysed before actual samples of interest [58].

Barnes et al. compared different gasoline samples by GC-MS and sequential peak ratio method and target ion response and observed that wood does not cause any interference in comparison process. They concluded that such comparisons are useful in comparing gasoline (extracted from debris) to unevaporated gasoline samples and in associating evaporated gasoline sample with its source and discriminate from other sources of gasoline [59].

Cavanagh-Steer et al. investigate the transfer and persistency of petrol on car carpets. They observed that evaporation level of petrol increases with rise in time between transfer and analysis and concluded that presence of petrol (fresh or slightly evaporated) in a significant amount on motor vehicles carpet is an indicative of addition of petrol to vehicle interior and eliminates the potential contamination due to normal vehicle usage [60].

Borusiewicz et al. studied the effect of different factors (type of burned material and accelerant, time of burning, availability of air) on the detection of traces of accelerants. No significant relationship between time of burning and accelerants traces detectibility was observed. They concluded that type of burned material causes highest interference in identification process while accelerant type and burning time is less significant. They also concluded that variation in air availability didn't significantly affect the detection of accelerants traces [61].

Borusiewicz and Zieba-Palus compared the adsorption efficiency of Tenax TA and Carbotrap 300 and concluded that Tenax TA is more effective for adsorption of non polar, high boiling compounds while Carbotrap 300 is more effective for adsorption of polar and volatile compounds [62].

Lu et al. compared the performance of differential mobility spectrometry (DMS) and mass spectrometry (MS) in the detection and classification of ignitable liquids from fire debris using projected difference resolution (PDR) and concluded that performance and efficiency of GC-MS is better than GC-DMS [63].

Montani et al. compared the efficiency of different matrices to collect the gasoline on suspects hands. They also developed the simple and effective sampling kit which was efficient in preventing external and cross contaminations. They concluded that non powdered latex gloves were most efficient and reliable in collecting residues of gasoline from suspect's hands and emit least interfering volatiles

[64].

Choodum and Daeid developed and validate a GC-MS method to analyse hydrocarbon residues encountered in fire debris samples. They also optimized the separation conditions such as carrier gas flow rate, column temperature programming and inlet temperature and concluded that present method is rapid, sensitive and provides better resolution than recommended National Centre of Forensic Science (NCFS) method for ignitable liquid analysis [65].

Prather et al. compared the simulated ignitable liquid residues to corresponding liquid in the presence of both evaporative losses and matrix interferences using multivariate statistical procedures such as Pearson Product Moment Correlation Coefficient (PPMC), Hierarchical Cluster Analysis (HCA) and Principal Component Analysis (PCA) and concluded that these statistical procedures can be used to associate ignitable liquid residues to liquid standards even in the presence of evaporation and matrix interferences but not to a specific level of evaporation [66].

Cacho et al. developed a novel method for the separation and identification of combustion accelerants in fire debris by GC-MS. Simple headspace sorptive extraction (HSSE) technique was used to preconcentrate the analytes. They also compared HSSE procedure with SPME procedure. 1g of debris was placed in 15ml glass vials for HSSE procedure. PDMS stir bar was exposed to vial headspace for 60 mins at 50^0C. Commercial stir bars coated with 0.5mm thick layer of polydimethylsiloxane were used as extracting phase. Thermal desorption unit (TDU) equipped with an autosampler and a programmed temperature vaporization (PTV) cooled injector system was used for sample introduction into GC. Limit of detection was in the range of 0.1-0.7ng/g depending on nature of particular accelerant. They concluded that HSSE procedure is more efficient and sensitive method than SPME and can be applied to extraction of accelerants from fire debris [67].

Muller et al. developed a simple, sensitive and innovative method for the identification of trace amounts of ignitable liquid residues on hands of suspect even after 3h of moistening. Method cannot distinguish between fuel used as an arson accelerant and fuel used for legitimate use [68].

Smale et al. compared the sensitivity and efficacy of different techniques used to extract ignitable liquid residue from concrete. Three of these techniques involve the covering of concrete surface with an absorbent material such as cat litter, absorbent matting and cotton pads while fourth technique uses Passive Headspace Residue Extraction Device (PHRED). In these techniques, absorbent material was applied to concrete and allowed to absorb any ignitable liquid residue for 1hr. The absorbed components were extracted using passive headspace extraction. PHRED was affixed directly to concrete surface and then evaporates ignitable liquid residue directly from concrete to charcoal strip within the device by heating. They concluded that PHRED is more sensitive and effective technique than cat litter in extracting ignitable liquid residue from concrete and it is portable [69].

Waddell et al. generates a clusters based on chemical composition of ignitable liquids by applying hierarchical cluster analysis on total ion spectrum data and classify them into 2 major groups: aliphatic and aromatic [70].

Multidimensional GC Methods

Jayatilaka and Poole [71] and Taylor et al [72]. identify petroleum distillates in simulated arson samples by multidimensional gas chromatographic method and concluded that present method is less influence by interfering co-eluting and matrix components and can be used to identify petroleum distillates in contaminated arson samples with improve certainty.

Pert et al. also advocate the utility of two dimensional GC (GC×GC) in the analysis of fire debris because it eliminates the interferences due to pyrolyzed products [10].

Conclusion

Test and control samples should be collected from crime scene and must be store in recommended containers in order to get valuable information from them. Both conventional and modern extraction procedures have their own merits and demerits and are used on the basis of availability. It is concluded that no single extraction method is universally effective for isolation of different petroleum products from variety of substrates of forensic importance.

Different spectroscopic methods used to analyse fire debris residues cannot provide the pin point identity of petroleum products due to their non specific nature.

However, these methods can be successfully used for screening purpose at initial stage of analysis.

Advances in instrumentation open the doors for utilization of more sophisticated analytical techniques in the analysis of fire debris residues. GC-MS is a well established technique for the analysis of fire debris residues due to its sensitivity, selectivity and reproducibility.

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Conflict of Interest

The authors declare that they have no conflict of interest.

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Review Article

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Forensic Applications of IR/FTIR

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Abstract

Infra-Red spectroscopy plays important role for analysis of several compounds, metals etc. Its use is readily understood from breadth of its applications. The range of material that can be analyzed by IR/FTIR is essentially unlimited. Applications are found in diverse fields such as forensic science, pharmaceuticals, food and agriculture, biological and clinical chemistry, environmental chemistry and many others.

Keywords: IR; FTIR; Dipole; Instrument etc.

Introduction

- Absorption of IR radiation by a molecule is the basis of this kind of spectroscopy
- It is also called absorption spectroscopy
- The extent of this absorption depends on the wavelength/frequency of the IR radiation passing through molecule and structure of the molecule.
- Absorption of radiation leads to a gain in the energy of the molecule.
- This gain in energy leads to a variety of vibrations (bond stretching, bending etc).
- In order to absorb IR radiation a molecule must go a net change in dipole moment because of its vibrational or rotational motion [1].
- No net change in dipole moment occurs during the vibration of homonuclear species such as O_2, N_2, H_2, and Cl_2 and hence these compounds do not absorb in the IR region.
- In recent years it has been proved that even the species such as O_2, N_2, H_2, and Cl_2 show slight IR absorption at high pressure, as a result of distortion during the collisions.
- IR spectroscopy has also been employed for quantitative analysis. However quantitative applications are of less significance than the qualitative applications.

Regions of the IR Spectrum

Different regions of the electromagnetic radiations are given in Table 1.

Table 1: Different regions of the electromagnetic radiations

Types of radiations	Limits (Wave length)	Wave number	Effect on the molecule}
1. Cosmic ray	0.0001 – 0.001 A^{o}	10^{12} cm^{-1}	Mossbauer (Change in nuclear transitions)
2. γ - rays	0.001 – 1 A^{o}	10^{10} cm^{-1}	
3. X-rays	1 – 10^{2} A^{0}		Change in core orbitals
4. UV i) for UV	100 – 200nm		
ii) Near UV	200 – 400nm		Change in electronic energy levels
iii) Visible	400 – 800nm	25000 – 12500 cm^{-1}	
5. IR i) Near IR	0.80μm - 2.5μm	12500 - 4000 cm^{-1}	Change in vibrational and rotational movement
ii) Mid IR	2.5μm - 15μm	4000 - 667 cm^{-1}	
iii) Far IR	15μm - 200μm	667 - 50 cm^{-1}	
6. Microwave	0.02 – 100cm		Change in rotational movement
7. Radio waves	1m – 100 m		Change in nuclear spin

1μm =1μ = 10^{3} nm = 10^{-4}cm
1 micrometer = 1 micron

IR Spectrum (Absorption Curve)

If a graph is plotted showing the variation of absorption of radiation (or % Transmission) by compound with wavelength or frequency or wave number, we get the absorption curve better known as IR Spectrum of the compound.

Principle

Since absorption of IR radiation by a molecule is the basis of this kind of spectroscopy. It is also called absorption spectroscopy. The extent of this absorption depends on the wavelength/frequency of IR radiation passing through the molecule and the structure of molecule. Absorption of radiation leads to a gain in the energy of the molecule. The gain in energy leads to a variety of vibrations (bond stretching etc) in the molecule.

Theory (Molecular Vibrations)

Absorption in the Infra-red region is due to the changes in the Vibrational and Rotational levels. When radiations with frequency range less than 100 cm^{-1} are absorbed, molecular rotation takes place in the substance. As this absorption is quantised, descrete lines are formed in the spectrum due to molecular rotation. Molecular radiations are set in, when more energetic radiation in the region 10^{4} to 10^{2} cm^{-1} are passed through the sample of the substance. The absorption causing molecular vibration is also quantised. Clearly, a single vibrational energy change is accompanied by a large number of rotational energy changes. Thus, the vibrational spectra appears as vibrational – rotational bands [2-6].

The vibrational – rotational bands, particularly those occurring between 4000 cm^{-1} and 666 cm^{-1} (2.5 – 15 μ) is of great importance in analytical chemistry. The frequency of wavelength of absorption depends upon:

a. The relative masses of the atoms

b. The force constants or bond strength and

c. The geometry of the molecule

Fundamental Vibrations: There are two fundamental vibrations

i) Stretching vibration

ii) Bending vibration

Stretching Vibration: In this type of vibrations, the distance between two atoms increases or decreases, but the atom remains in the same bond axis. There are two types of stretching vibrations.

a. Symmetric Stretching: in this type of stretching, the movement of atoms with respect to a particular atom in a molecule is in same direction (Figure 1).

Fig. 1: Symmetric stretching

b. Asymmetric Stretching: In these vibrations one atom approaches the central atom while the other departs from it (Figure 2).

Fig. 2: Asymmetric Stretching

Bending Vibration: In this type of vibrations, the position of atom changes with respect to the original bond axis. Bending vibrations are of four types (Figure 4)-

(i) Scissoring: In this type, two atoms approach each other.

(ii) Rocking: In this type, the movement of the atoms takes place in the same directions.

(iii) Wagging: Two atoms move up and below the plane with respect to the central atom.

(iv) Twisting: In this type, one of the atoms moves up the plane while the other moves down the plane with respect to the central atom.

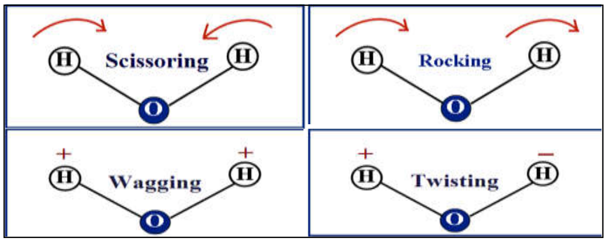


Fig. 3: Scissoring, Rocking, Wagging and Twisting

Number of Fundamental Vibrations: Poly-atomic molecules may exhibit more than one fundamental vibrational absorption bands. The number of these fundamental bands is related to the degree of freedom in a molecule. The number of degree of freedom is equal to the sum of the co-ordinates necessary to locate all the atoms of a molecule in space. Each atom has three degree of freedom corresponding to the three cartesian co-ordiantes (x, y, z) necessary to describe its position relative to other atoms in a molecules.

An isolated atom which is considered as a point mass has only translational degree of freedom. It can not have vibrational and rotational degree of freedoms.

When atoms combine to form molecule, no degree of freedom are lost. Hence total number of degree of freedom = 3n, where n= number of atoms in a molecule. A molecule which is of finite dimensions will thus be made up of rotational, vibrational and translational degree of freedom. So, 3n degree of freedom = Translational + Rotational + Vibrational

Rotational degree of freedom result from the rotation of a molecule about an axis through the centre of gravity. Since we are concerned only with the number of fundamental vibrational modes of a molecule, so we calculate only the number of vibrational degree of freedom of a molecule. Since only three co-ordinates are necessary to locate a molecule in space, we say that a molecule has always three translational degree of freedom (Table 2).

Table 2: Vibrations of Linear Molecule

For A Linear Molecule of N Atoms:	
Total degree of freedom	3n
Translational degree of freedom	3
Rotational degree of freedom	2
Vibrational degree of freedom	(3n – 3 – 2)= (3n–5)

Hence theoretically there will be (3n–5) possible fundamental bands for the linear molecules.

For Example CO_2 (Linear Shaped Molecule)

Number of atoms (n) = 3

Total degree of freedom = 3n = 3×3 = 9

Translational degree of freedom = 3

Rotational degree of freedom = 2

Vibrational degrees of freedom = 9 – 3 – 2 = 4

Hence, for carbon dioxide molecule, the theoretical number of fundamental bands should be equal to four.

For Non-Linear Molecule of N Atoms:

Total degree of freedom = 3n

Translational degree of freedom = 3

Rotational degree of freedom = 3

Vibrational degree of freedom = (3n–3–3)=(3n–6)

For example benzene, C_6H_6

Number of atoms (n) = 12

Total degree of freedom = 3n = 3×12 = 36

Translational degree of freedom = 3

Rotational degree of freedom = 3

Vibrational degrees of freedom = (36 – 3 – 3) = 30

So theoretically there should be 30 fundamental bands in the infra-red spectrum of benzene. It has been observed that the theoretical numbers of fundamental vibrations are seldom obtained. It is because of following reasons:

i. Fundamental vibrations that fall outside the region under investigation, i.e. 2.5 to 15 µ.

ii. Fundamental vibrations are too weak to be observed as bands.

iii. Fundamental vibrations are so close that they overlap i.e. exists as degenerate vibrations.

iv. Certain vibrational bands do not appear for the required change in the dipole-moment in a molecule.

Various Types of Spectra Given by Molecular Species

1. *Nuclear magnetic resonance (NMR) spectra*, which arise from transitions between the nuclear spin energy levels of a molecule in the applied magnetic field.
2. *Nuclear quadrupole resonance (NQR) spectra*, which result from the transitions between the nuclear spin energy level of a molecule arising from the interaction of the unsymmetrical charge distribution in nuclei with the magnetic field.
3. *Electron spin resonance (ESR) spectra*, which arise from transition induced between the electron spin energy levels of a molecule in an applied magnetic field. It is also called electron paramagnetic resonance spectra (EPR).
4. *Rotational or microwave spectra*, which result from transitions between the rotational energy levels of a gaseous molecule on the absorption of radiation falling in the microwave region. The microwave spectra occur in the range 1-100cm^{-1}.
5. *Vibrational and vibrational rotational spectra* originate from transitions induced between the vibrational energy levels of a molecule on the absorption of radiation belonging to infra-red region and generally occur in the range 200-4000 cm^{-1}
6. *Raman spectra* are also related to vibrational and /or rotational transitions in a molecule but in a different manner. In this case, scattering and not the absorption of radiation is measured.
7. *Electronic spectra* arise from electronic transition in a molecule by the absorption of radiation in the visible and ultra violet regions.
8. *Mossbaur spectra* result from absorption of very high energy γ- photons of frequency about 10^{13}MHZ by the nuclei. These spectra are therefore also known as γ- ray spectra.
9. *Photo electron spectra (PES)* arise when a beam of photons of known energy is allowed to fall on the sample and the K.E. of the ejected electron is measured.

Force Constant: In a harmonic oscillator, the resonating force per unit displacement is called force constant F and is given by the equation:

$$F = 4\Pi^2 \nu^2 c^2 \left(\frac{m_1 m_2}{m_1 + m_2} \right)$$

where ν is vibrational frequency, m_1 and m_2 are masses of oscillating atoms, and c is velocity of light.

The force constant for diatomic molecule can be obtained by using above equation provided the value of w is known.

Force constants of some bonds in dynes cm^{-1} are as follows:

Table 3: Vibrational frequencies of different functional groups.

Bonds	C-O	C=O	C-N	C=N	C≡N	C-C	C=C	C≡C
Force Constant ×10^5	4.9	12.3	4.8	12.1	17.5	4.6	9.5	15.8

Calculation of Vibrational Frequencies

One may calculate the region of vibration for a diatomic molecule by applying Hookes' law; the frequency of vibration is directly proportional to the square root of theforce constant of the bond (Table 3). This implies that stronger is bond greater will be frequency of absorption. Further wave number (λ^{-1}), frequency (ν) and energy (E) are directly proportional to each other however; wave length (λ) is inversely proportional to energy. Mathematically Hookes' law is expressed as:

$$\bar{\nu} = \frac{1}{2\Pi C}\sqrt{\frac{F\,(m_1 + m_2)}{m_1 m_2}}$$

where $\bar{\nu}$ is wave number (cm^{-1}), c = velocity of light (cm sec^{-1}), F = Force constant (dyne cm^{-1} or g sec^{-2}), m_1, m_2 are masses of atoms.

For example, the region of $^{12}C—^{1}H$ stretching frequency may be calculated as:

$$\bar{\nu} = \frac{1}{2 \times 3.142 \times 2.998 \times 10^{10}} \left[5 \times 10^{5} \times \frac{\dfrac{12}{6.023 \times 10^{23}} + \dfrac{1}{6.023 \times 10^{23}}}{\dfrac{12}{6.023 \times 10^{23}} \times \dfrac{1}{6.023 \times 10^{23}}} \right]^{1/2}$$

$$\bar{\nu} = 3032\ cm^{-1}$$

actual range for C-H stretching is 2850-3000 cm^{-1}

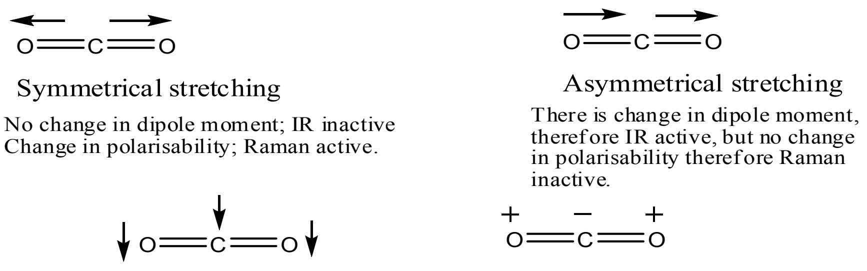
Differences between IR and Raman Spectroscopies

There are several Differences between IR and Raman IR and Raman. Major are enclosed in Table 4.

Table 4: Differences between IR and Raman

Raman	IR
It is due to scattering of light by the vibrating molecule.	It is due to absorption of light by the vibrating molecule.
It is not necessary for a molecule to possess a permanent dipole moment.	In this case molecule must possess a permanent dipole moment.
In this case water can be used as solvent. intense absorption peak in IR.	Water can't be used as solvent due to its
The vibration in Raman is active if it causes change in polarisability.	Vibration in IR is active, which causes change in dipole moment.
Sample can be in any physical state.	Gaseous samples can rarely be used.
It gives an indication of covalent character in molecules.	It gives an indication of ionic character in molecules.
The cost of instrumentation is high.	The cost of instrumentation is comparative ely low

Mutual Exclusion Principle: It states that in a molecule with centre of symmetry, vibrations that are Raman active are IR inactive and vice-versa. In molecules with different elements of symmetry, certain bands may be active in IR, Raman, both or neither. For a complex molecule with no symmetry, all of the normal modes are active in both IR and Raman, but their observance may or may not exist [7-8]. A simple molecule which obeys this principle is CO_2. Carbondioxide has an inversion centre or centre of symmetry. Its different active modes in IR and Raman spectroscopy are indicated below in scheme 1.



Symmetrical stretching

No change in dipole moment; IR inactive
Change in polarisability; Raman active.

Asymmetrical stretching

There is change in dipole moment, therefore IR active, but no change in polarisability therefore Raman inactive.

In plane bending

Out of plane bending

The bending vibrations of CO_2 are degenerate (having same energy) and appear in the same region (666 cm^{-1}) in the IR. Further these bands are Raman inactive due to no change in polarisability.

Scheme 1: Different vibrational modes in symmetrical CO_2 molecule

Instrumentation

The FTIR consists of following major parts:

1. Source of IR Radiation
2. Cell compartment
3. Grating
4. Detector

Systematic representation of parts of FTIR are given in Figure 4.

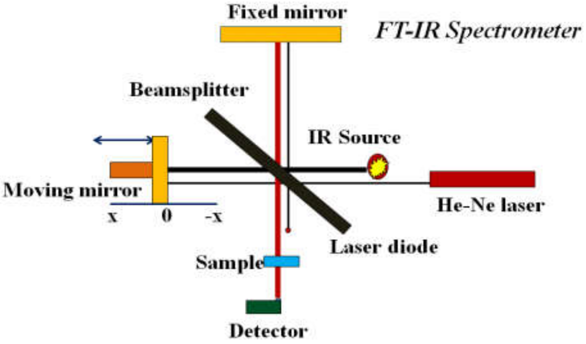


Fig. 4: Systematic representation of parts of FTIR instrument

Source of IR Radiation

Common source in the IR is the Nernst Glower consisting of a mixture of zirconium oxide, ytterbium oxide and erbium oxide heated electrically to about 1500 °C. More intense source consisting of a silicon carbide source (Globar) has also been introduced in modern IR Spectrometers.

Cell Compartment

It houses cells in which the sample under examination is placed. These cells are usually made of rock salt (NaCl), but materials like KBr, CaF_2, CsBr, AgBr etc are also used occasionally. The glass cells being opaque to IR radiation cannot be used [9]. These cells are normally stored in a desicator when they are not in use. Cells are usually cleaned in carbon tetrachloride. Water must be avoided since it can dissolve out the cell windows made of rock salt.

Grating

While NaCl prisms served as monochromators (which convert a broad spectrum of light into monochromatic components) in older spectrometers, diffraction grating is used in modern spectrometers to serve the same function. Lights of different wavelengths can be obtained by rotating the grating relative to the light source.

Detector

A variety of detectors are in use. They may simply be thermocouples whose e.m.f. changes with the radiation falling on them. A Golay detector consists of a sealed cell of xenon gas, a blackened metal plate for the radiation to fall on and a silvered diaphragm. The detector responds to the difference in intensity between the light beams coming from reference and the sample cells.

Some Important Points for Proper Maintenance of IR Spectrophotometer

1. IR cells are normally stored in desiccators when they are not in use.
2. Cells are usually cleaned by carbon tetrachloride, water must be avoided since it can dissolve out the cell windows of rock salt.
3. Hydroxylic solvents like water and alcohol should be avoided as they would not only dissolve out the cell made of rock salt but would also give overlapping bands in certain cases.

Sampling

Gaseous Substance: Gaseous substances are examined as such in specially designed gas cells.

Liquid Substances: Liquid substances are examined in the form of a thin film placed between the rock salt plates of a liquid cell. A drop of the liquid substance is placed on a rock salt plate of the liquid cell and then the other plate of the cell is placed on it so that liquid forms a thin film between two plates

Solid Substances: Solid substances are examined in the form of a pellet or a mull or a solution in a suitable solvent (Figure 5).

Fig. 5: Preparation of sample

a. As pellets: The solid substance (few mg) is mixed thoroughly with carefully dried spectroscopic grade KBr (~ 0.5g) in a gate pestle mortar. The mixed powder or a minipress to get a pallet that is sufficiently transparent. The pellet is then placed in IR sample holder for examination (Figure 6).

Fig. 6: Part of FTIR for preparation of sample

b. As Mulls: The mulling liquid commonly employed is nujol (a highly purified mineral oil). Nujol can sometimes be replaced by liquids such as fluorolube (a chlorofluoro hydrocarbon), hexachlorobutadiene etc. The substance, mixed with nujol, is thoroughly mulled in an agate pestle mortar. A drop or two of the resulting mull is then examined as described earlier under liquid substances. It may be noted that nujol itself has IR bands around 2900 and 1400 cm^{-1} (Figure 7).

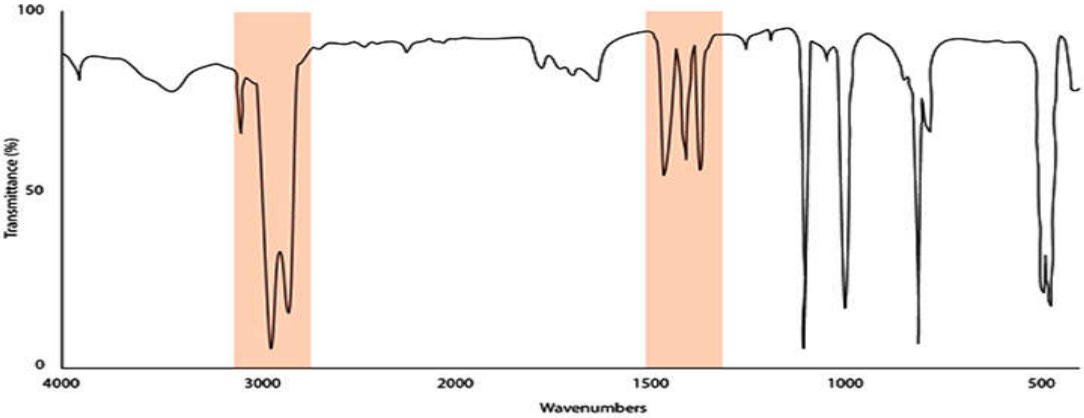
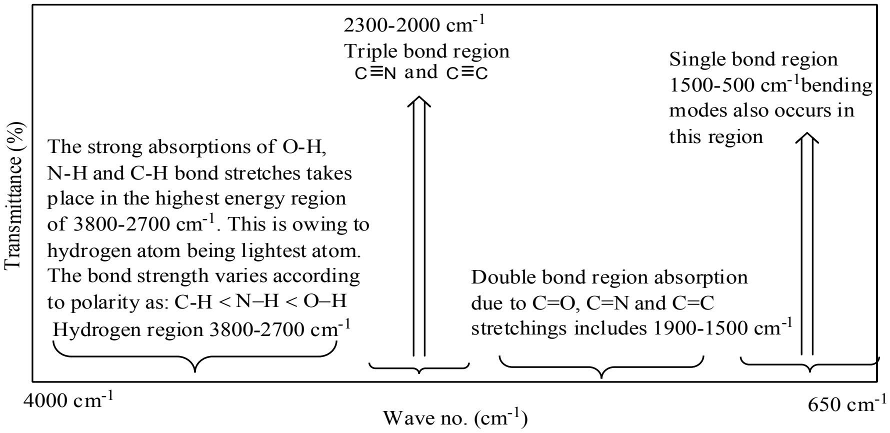


Fig. 7: The IR bands of nujol

c) As solutions: IR spectra of solid can be obtained by dissolving solid into suitable liquid. The solvent to be used must be of spectroscopy grade, must dissolve the solid and must be transparent in most of the mid-IR region. No one solvent is transparent in the entire region and the solvent has to be selected with regard to the region where the compound under study is expected to have IR bands. The most popular solvent for IR spectroscopy are CCl_4, CS_2 and $CHCl_3$. CCl_4 has band only at 700-850 cm^{-1}, CS_2 has bands at 1400-1600 cm^{-1} and 2100-2200 cm^{-1} only and $CHCl_3$ has bands at 600-806 cm^{-1} and 1175-1200 cm^{-1}. Hydroxylic solvents like water and alcohol should be avoided as they could not only dissolve out the cell made of rock salt but would also give overlapping bands in certain cases.

Important Regions of IR Spectrum

There are three important region of I. R. spectrum. 1. Functional group region (4000-1300 cm^{-1}) 2. Fingerprint region (1300-900 cm^{-1}) and 3. Aromatic region (900-650 cm^{-1}), Scheme 2.



1500-500 cm^{-1}bending modes also occurs in this region

The strong absorptions of O-H, N-H and C-H bond stretches takes place in the highest energy region of 3800-2700 cm^{-1}. This is owing to hydrogen atom being lightest atom. The bond strength varies according to polarity as: C-H < N–H < O–H

Hydrogen region 3800-2700 cm^{-1}

Double bond region absorption due to C=O, C=N and C=C stretchings includes 1900-1500 cm^{-1}

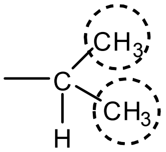
Scheme 2: Representation of different regions of IR spectra.

Functional Group Region

The region of 4000-1300 cm^{-1} is called functional group region. It consists of several functional groups like unsaturation, alcohols, aldehydes, ketones, esters, acids, amides, amines etc. which are discussed as follows.

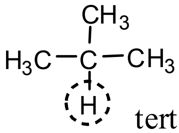
Alkanes

1. C–H stretching bands = 2900 cm^{-1} (Figure 8).
2. C–C stretching bands = 1400 cm^{-1}
3. A doublet (two bands of approximately equal intensity) between 1370-1380 cm^{-1} for gem-dimethyl group.



geminal dimethyl groups

4. Tertiary hydrogens in alkanes show a number of bands in fingerprint region (1300-900 cm^{-1})



tertiary hydrogen

5. Functional groups with chain shorter than four carbons show bands which may be diagnostic. For example:

Propyl chain CH_3-CH_2-CH_2- (745–735 cm^{-1})

Ethyl chain CH_3–CH_2- (790–770 cm^{-1})

6. The strong band at 725 cm^{-1} indicates the rocking Vibrational mode of a chain of methylenes longer than four carbon atoms.

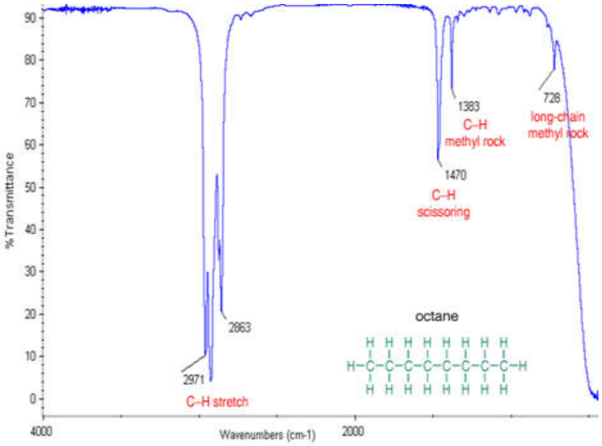


Fig. 8: IR spectra of normal octane.

Alkenes

1. The C-H stretching bands in alkenes appear at a slightly higher frequency (around 3000 cm^{-1}) than alkanes.
2. C-H stretching band at 3000 cm^{-1} or slightly above this frequency is characteristic of unsaturation.
3. C=C stretching band in alkenes is also at a higher frequency (1600-1700 cm^{-1}) than in alkanes and this band is weak to medium (Figure 9, 10).

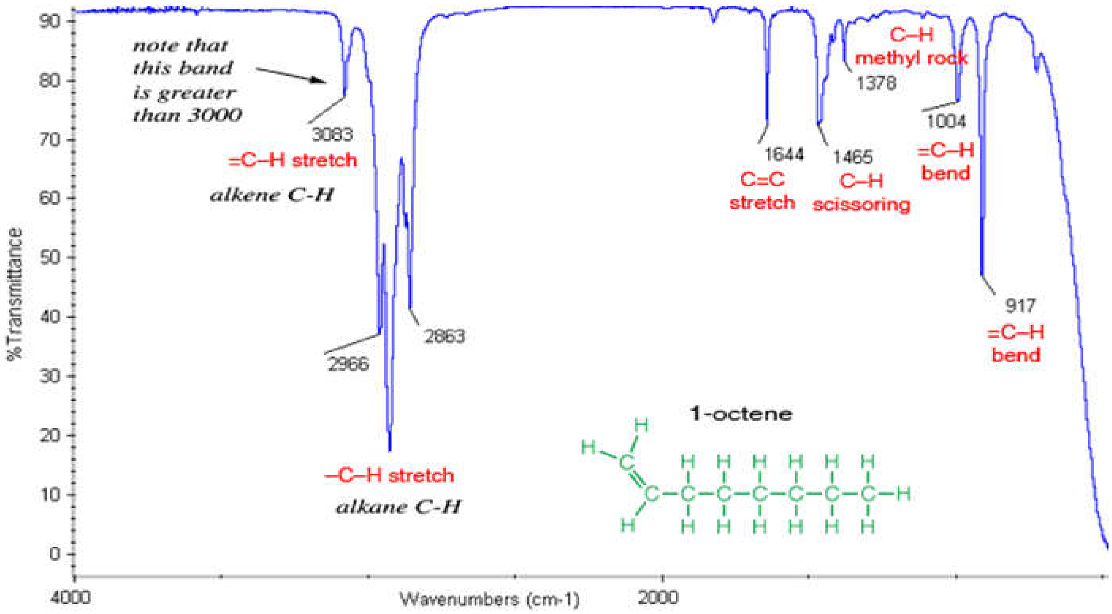


Fig. 9: IR spectra of 1-octene.

4. Extent of substitution of the double bonds are:

$RCH=CH_2$	1645 cm^{-1}
$R_2C=CH_2$	1655 cm^{-1}
RCH=CH R (cis)	1660 cm^{-1}
R CH=CH R (trans)	1675 cm^{-1}
Tri & Tetra substituted	1670 cm^{-1}

The intensity of this band decreases gradually from medium to weak with increasing substitution of the double bond.

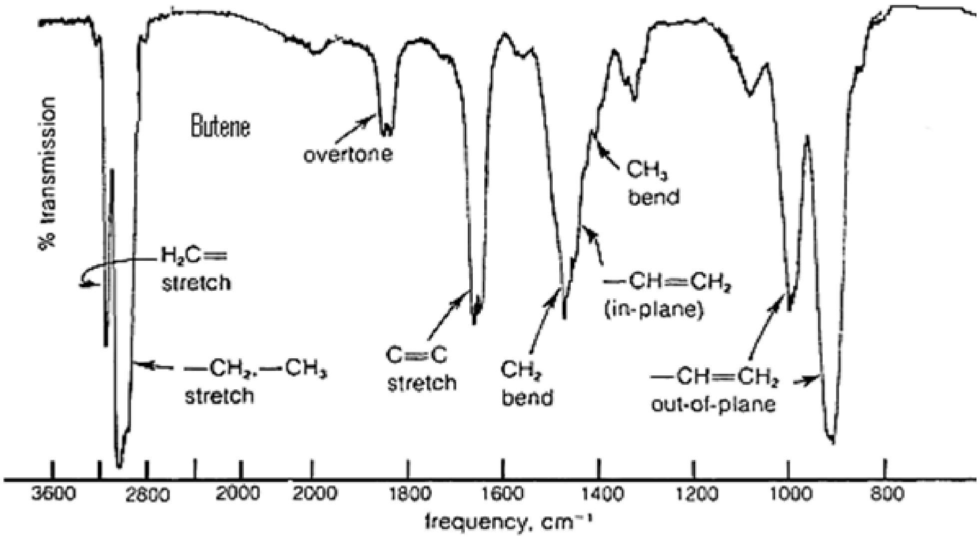


Fig. 10: IR spectra of Butene

Alkynes

1. C–H stretching band in alkynes is at still higher frequency (3310-3270 cm^{-1}) than in alkens and alkanes
2. The Ca”C stretching band in alkynes is fairly weak and appears at 2300-2100 cm^{-1} depending on the location of triple bond (Figure 11). For example

External C≡C	2150-2100 cm^{-1}
Internal C≡C	2250-2200 cm^{-1}

3. It may be noted that symmetrically substituted alkynes say $CH_3–C\equiv C–CH_3$ shows no stretching band at all.

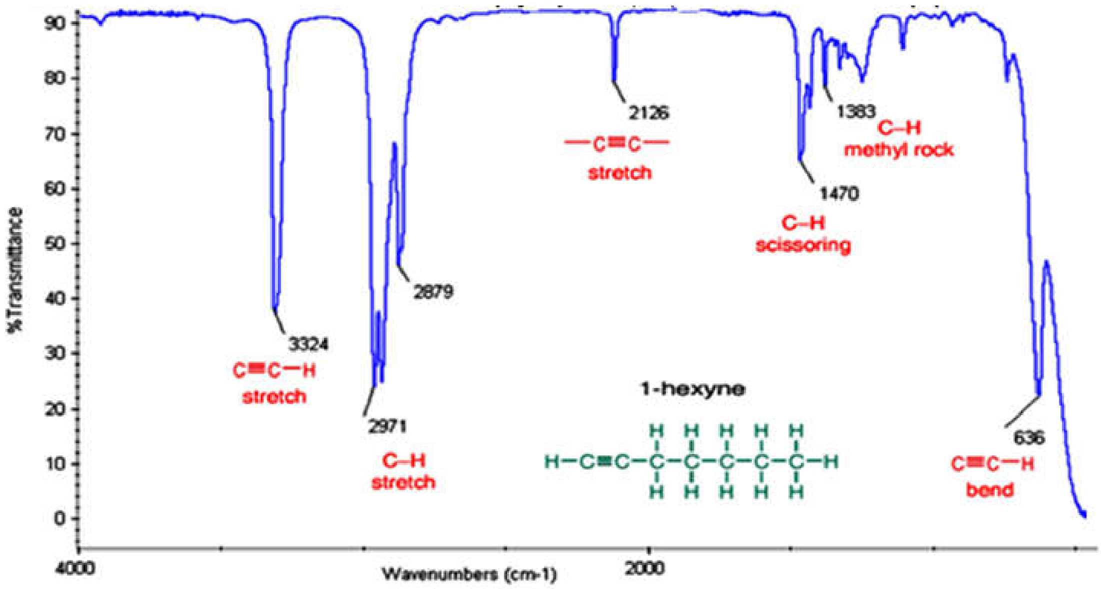


Fig. 11: IR spectra of 1-hexyne

Alicyclic Hydrocarbons

1. Cycloalkanes and cycloalkenes do not show any unique band compared to alkanes/alkenes. Cyclopentane and cyclohexane for example show C–H stretching bands around 2900 cm^{-1}
2. The cyclopropane ring, however, is so strained that it shows a C–H stretching band charactaristic of unsaturated bands around 3100-3000 cm^{-1}

Alcohols

1. Alcohols show a broad intense band at 3650-3500 cm^{-1}. The narrow range in which this band appears gives idea about the class to which an alcohol belongs.

   3640-3630 cm^{-1} Primary alcohol (Figure 12), 3625-3620 cm^{-1} Secondary alcohol (Figure 13) and 3620-3610 cm^{-1} Tertiary alcohol (Figure 14).
2. When IR spectra of alcohols are taken in gaseous form or in very dilute solutions (alcohols mostly exist in the free form) the above bands are observed.
3. When IR spectra of alcohols are taken in liquid films or pallets or concentrated solutions, the precise position depending on relative proportion of the hydrogen bonded form sometimes both peaks at about 3650 cm^{-1} and 3350 cm^{-1} corresponding to 'free' and hydrogen bonded forms respectively appear. That is due to hydrogen bonding the IR band broadens and reduces to its lower value.
4. Alcohols also show strong C–O stretching bands at 1000-1150 cm^{-1}. The precise position of this band varies with the class of the alcohol.

   1150-1100 cm^{-1}, Secondary (2°) & Tertiary (3°) alcohols, 1060-1020 cm^{-1}, Primary (1°) alcohols 1066-1010 cm^{-1} cyclic alcohols.
5. *Distinction between intermolecular and intramolecular hydrogen bondings:* The dilution effect may distinguish the intermolecular and intra molecular hydrogen bondings; while testing solution is successively diluted the intramolecular hydrogen bonding remains unaffected however intermolecular hydrogen bonding weakens. Thus concentrated solution of alcohol or phenol causes the sharp band around 3600 cm^{-1} to be replaced by a broad and less intense frequency band due to intermolecular hydrogen bonding. Thus in a nut shell non hydrogen bonded (free) hydroxyl group yields a sharp band at higher frequency and hydrogen bonded hydroxyl group results abroad band at lower frequency (3360 cm^{-1}) region.

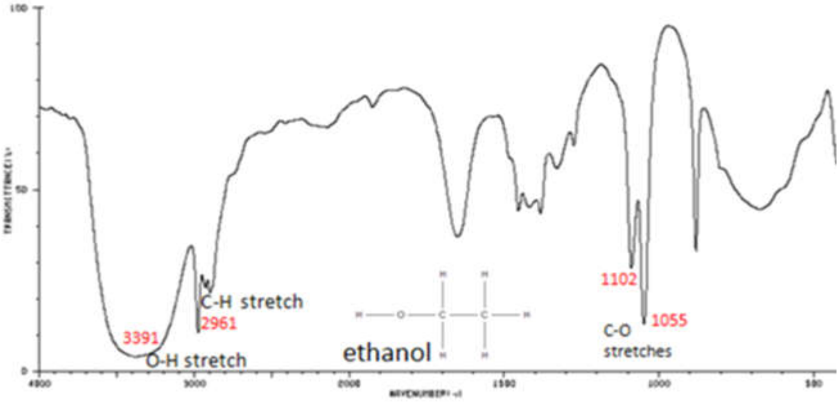


Fig. 12: IR spectra of ethanol

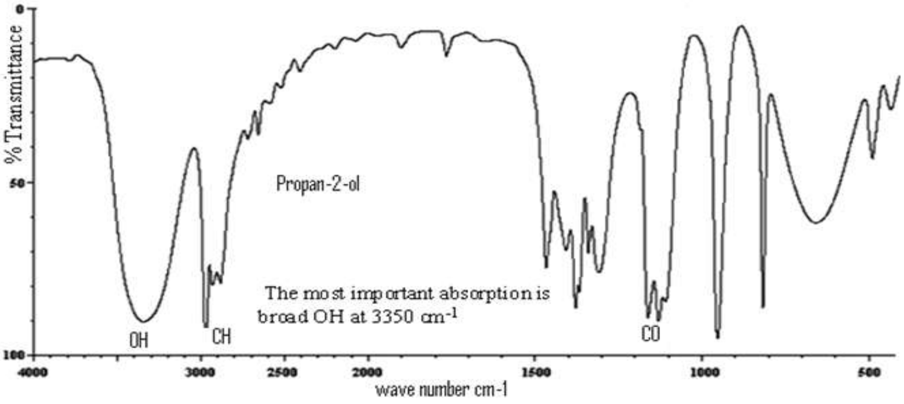


Fig. 13: IR spectra of Propan-2-ol

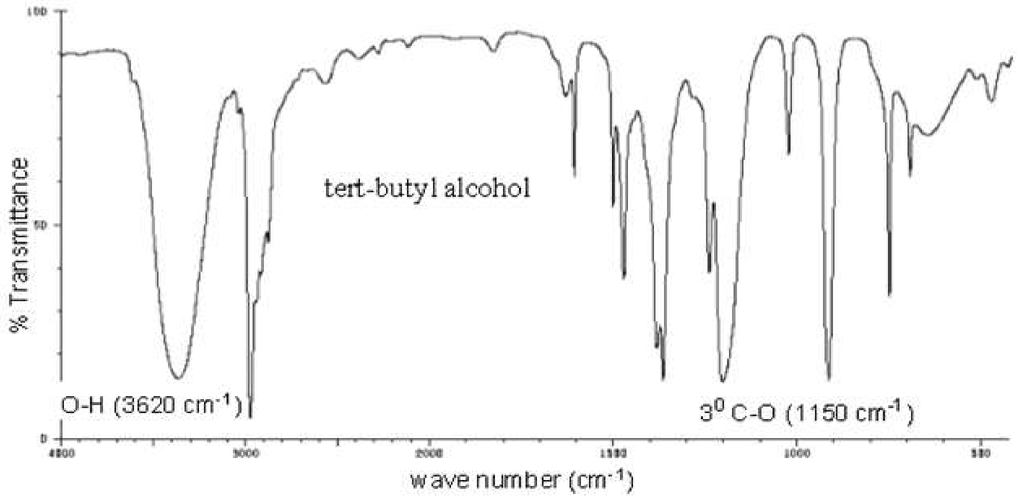


Fig. 14: IR spectra of 2-methylpropan-2-ol.

Ethers

1. They show characteristic C-O stretching bands for various alkoxy groups (Figures 15, 16). For example

-OCH_3 (1190 cm^{-1}), -OCH_2CH_3 (1150, 1100 cm^{-1}), -O- iPr (1175, 1135, 1110 cm^{-1}), -O-n-Bu (1150, 1125, 1075 cm^{-1}), -O-t-Bu (1200, 1150, 1050–1000, 920–820, 770–720 cm^{-1}).

2. In addition, methyl ethers show a strong characteristic methyl stretching band at 2830–2810 cm^{-1}

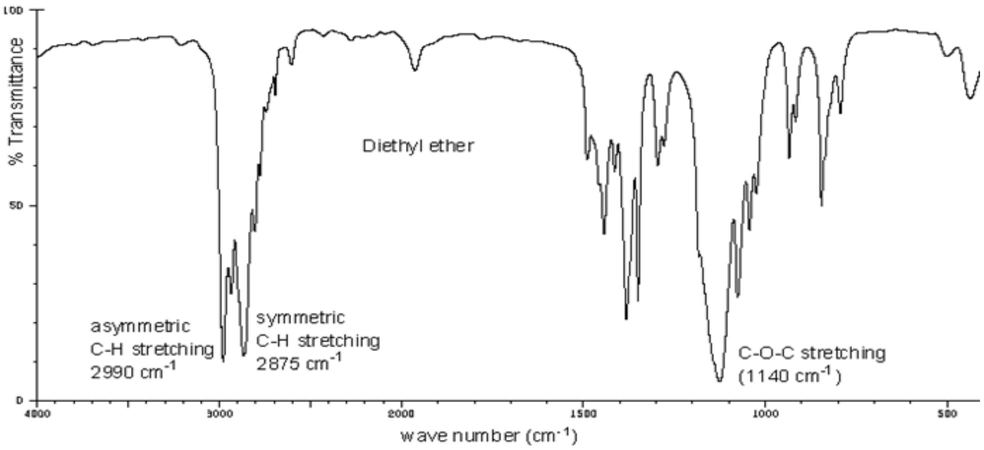


Fig. 15: IR spectra of diethyl ether

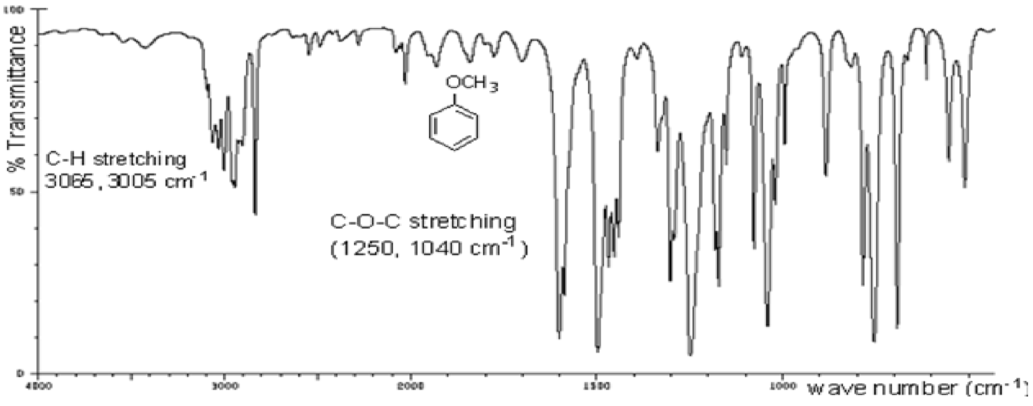


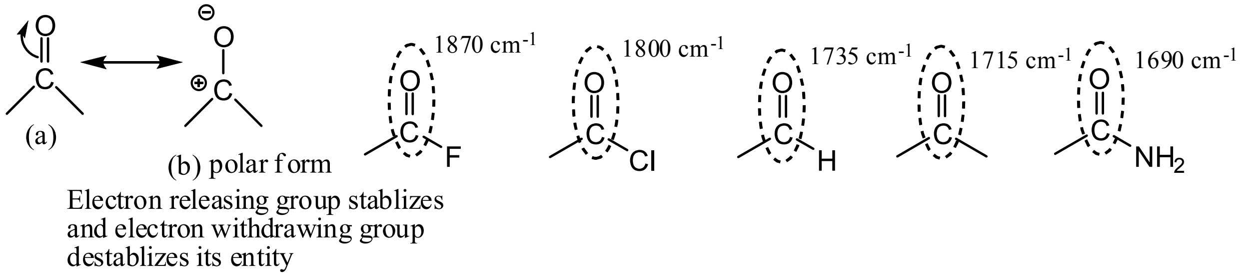
Fig. 16: IR spectra of methoxybenzene

Carbonyl Compounds

Carbonyl compound show a strong sharp band around at 1900-1580 cm^{-1} (Figure 17-20). However, the precise position depending on the nature of parent compound as below:

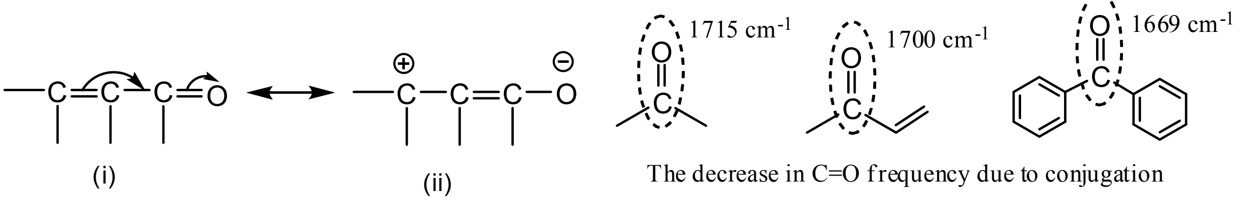
Ketones: Ketones show a strong sharp carbonyl band around 1700 cm^{-1}. There are, however, characteristic shifts in the position of this band depending on the structural environmental as given below (Figures 17-20):

(i) Inductive and Mesomeric Effects: Electron pulling groups decreases the stability of polar contributing form of carbonyl group (b) with an effective increase in double bond character. This causes increase in frequency of absorption for C=O. Conversely an electron pushing group stabilizes the polar form of carbonyl group by mesomeric effect and hence reduces its value (Scheme 3).



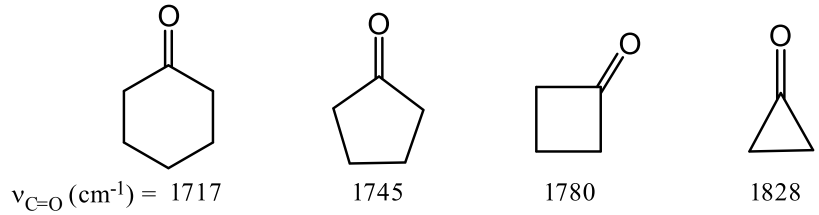
Scheme 3: C=O stretching values for different substituents.

(ii) Conjugation Effect: Conjugation of carbonyl group with double bond (olefinic or aromatic ring) causes delocalization of ð electrons of both C=C bond and C=O bond. This results dwindling of carbonyl stretching frequency from 1717 cm^{-1} to 1690 cm^{-1} and C=C stretching from 1645 cm^{-1} to 1620 cm^{-1}. This lowering is attributed to resonance as represented below (Scheme 4):



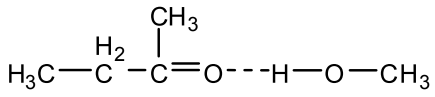
Scheme 4: Resonance and C=O stretching values for á, â-unsaturated ketones.

(iii) Ring Strain Effect: As the ring size decreases angle strain increases and these results increase in the C=O stretching frequency (Scheme 5). The normal value of cyclic carbonyl system is for cyclohexanone (í$_{C=O}$ = 1717 cm^{-1}). This effect is due to the increased interaction between the carbonyl double bond and the associated neighbouring single bonds. This increased interaction, as the ring size reduces causes resistance to the motion of the carbon of carbonyl group during stretching vibrations and thus increases force constant.



Scheme 5: The effect of angle strain on carbonyl stretching vibration.

(iv) Effect of Solvent: Intermolecular hydrogen bonding between a ketone and an alcohol (solvent) causes a slight decrease in the frequency of carbonyl group (Scheme 6). For example a neat sample of 2-butanone absorbs at 1715 cm^{-1} whereas its 10% solution in methanol absorbs at 1706 cm^{-1}.


$H_3C-\overset{H_2}{C}-\overset{CH_3}{C}=O\cdots H-O-CH_3$

Intermolecular hydrogen bonding between solvent (alcohol) and compound (ketone)

Scheme 6: Hydrogen bonding between methyl ethyl ketone (sample) and alcohol (solvent)

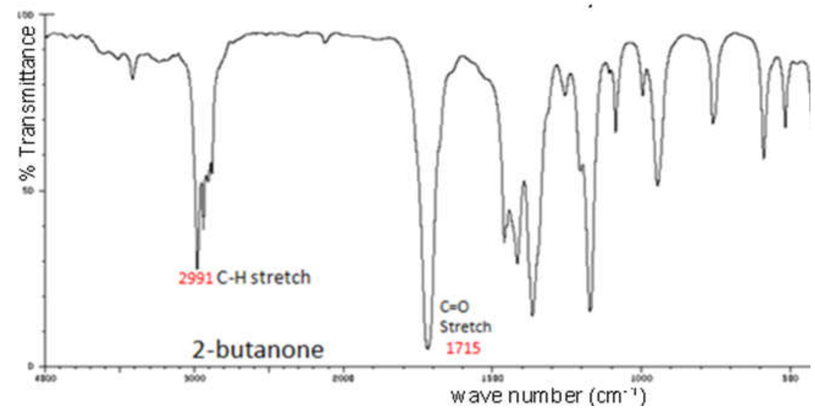


Fig. 17: IR spectra of Butan-2-one

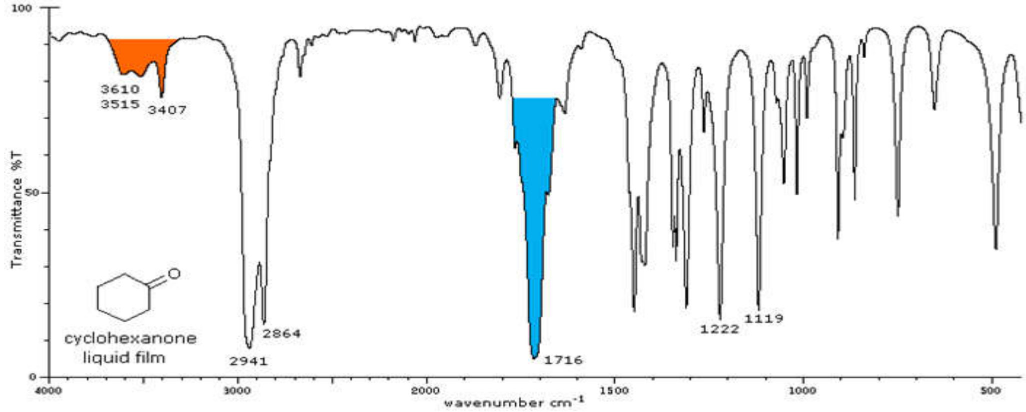


Fig. 18: IR spectra of cyclohexanone

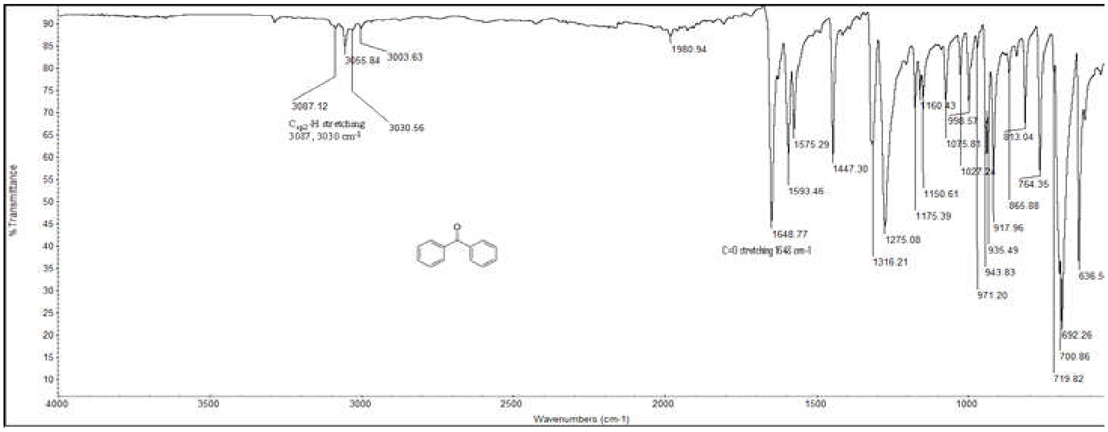


Fig. 19: IR spectra of Benzoquinone

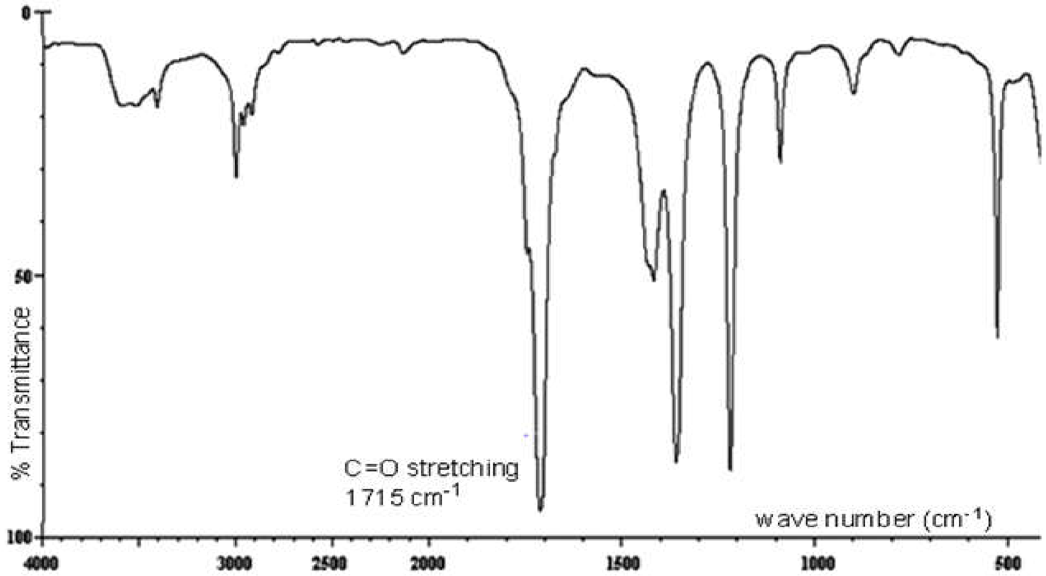


Fig. 20: IR spectra of acetone

$CH_3COCH_2CH_3$ (1715 cm^{-1}), $CH_3COCH=CH_2$ (1680 cm^{-1}).

From the above it is clear that:

1. The more is electron withdrawing group, the higher is the frequency of carbonyl band.
2. The more is electron releasing group, the lower is the frequency.
3. Conjugation decreases the frequency of carbonyl band.
4. The more strained is the cyclic ring then higher is the frequency of carbonyl band.

Quinones

1. Quinones are specific examples of á, â-unsaturated carbonyl compounds exhibit characteristic band due to C=O stretching in the range of 1690-1635 cm^{-1} (Figure 21).
2. If carbonyl group is in the other aromatic ring (pyren quinone), C=O stretching further reduces in the range of 1655-1635 cm^{-1} due to extended conjugation.

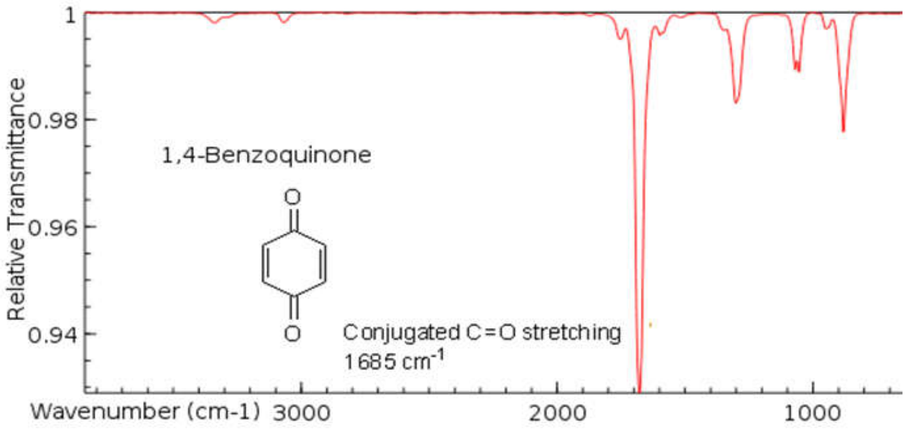


Fig. 21: IR spectra of 1,4-Benzoquinone

b. Aldehydes

1. Aldehydes show the carbonyl band at about 10-15 cm^{-1}; high value to the corresponding ketones. This is due to large +I effect operating in ketones as compared to aldehydes.
2. Conjugative effects on the position of the carbonyl

band in aldehydes are similar to those observed in ketones.

3. Aldehydes show a characteristic C–H stretching band around 2730 cm^{-1} and 2740 cm^{-1} (Figure 22).

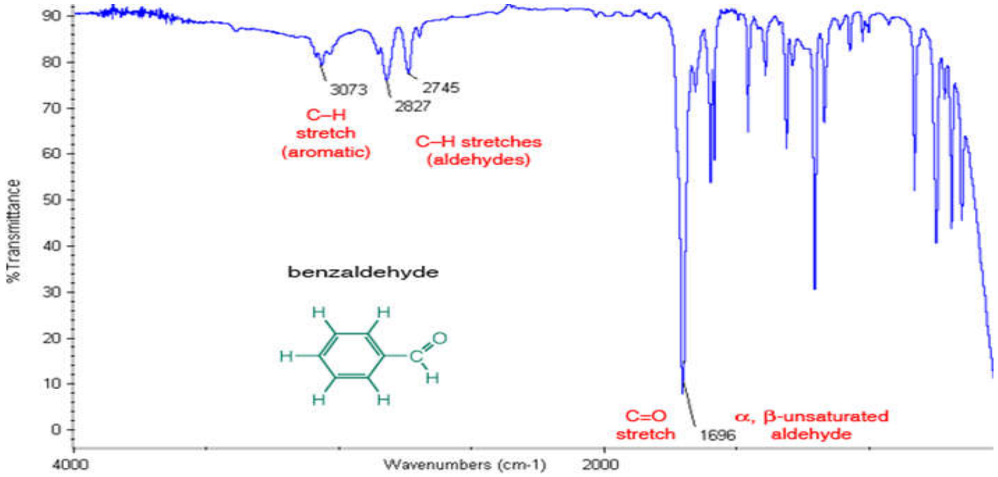
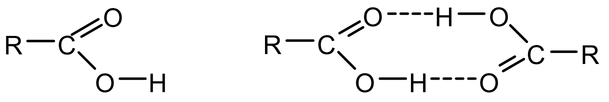


Fig. 22: IR spectra of Benzaldehyde.

c. The C=O bands in Carboxylic Acids:

1. Carboxylic acids generally exist as dimers in the solid state, but in dilute solution they exist mostly in monomeric state (Scheme 7).



(monomer: in dilute solution)
ν =1750 cm^{-1}

(dimer: in solid state or conc. solution)
ν =1700 cm^{-1}

Scheme 7: Presentation of monomeric and dimeric carboxylic acids.

2. The monomeric acid shows the carbonyl abnd at 1750 cm^{-1} and dimeric acid at 1700 cm^{-1} [10-13].

3. Since dimeric form has strong hydrogen bonding, the O–H stretching band shifts to lower frequency at 2700-2500 cm^{-1}. In the less common monomeric form, however, the O–H stretching band appears around 3500 cm^{-1} (Figure 23).

4. In addition, carboxylic acids show coupled C–O & O–H stretching at 1420 & 1300 cm^{-1}.

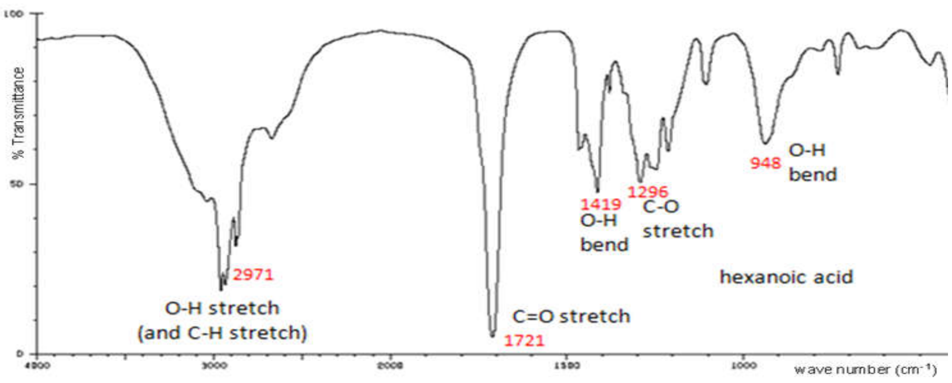


Fig. 23: IR spectra of Hexanoic acid.

d. **Esters**

1. The carbonyl band in esters appears at frequency higher than that observed in ketones (Figure 24). For example,

$CH_3\ COO\ C_2H_5$	$CH_3\ CO\ CH_3$
Ethyl acetate	Acetone
Carbonyl band appears between 1755-1740 cm^{-1}	Carbonyl band appears at 1715 cm^{-1}

2. In addition, C–O stretching band appears in 1280–1000 cm^{-1}.

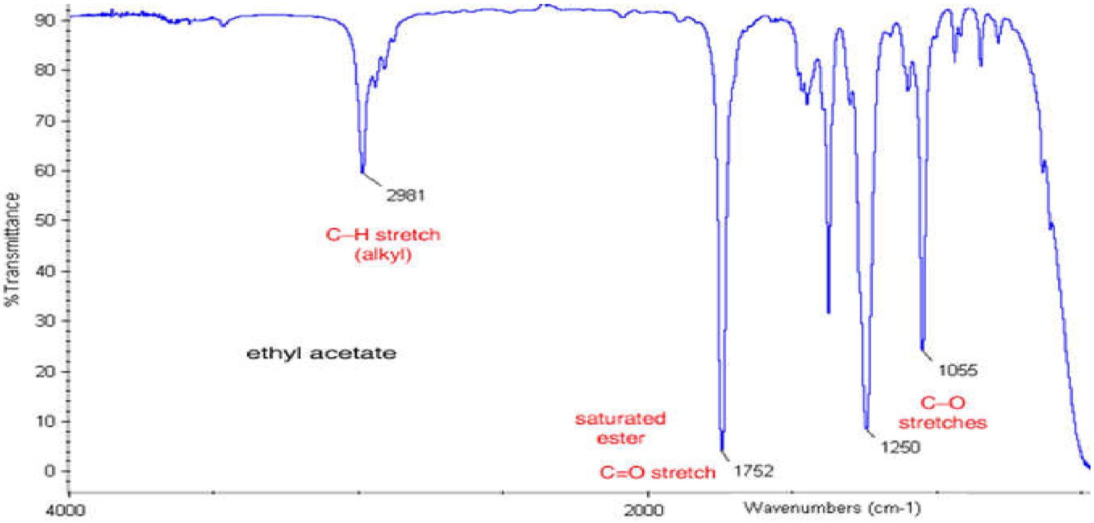


Fig. 24: IR spectra of Ethyl acetate

3. In aromatic ester viz, ethylbenzoate C-H stretch (aromatic) appears at 3078 cm^{-1} and C-H stretch (alkyl) at 2986 cm^{-1}, carbonyl stretch at 1726 cm^{-1} and C-O stretch at 1117 cm^{-1} (Figure 25).

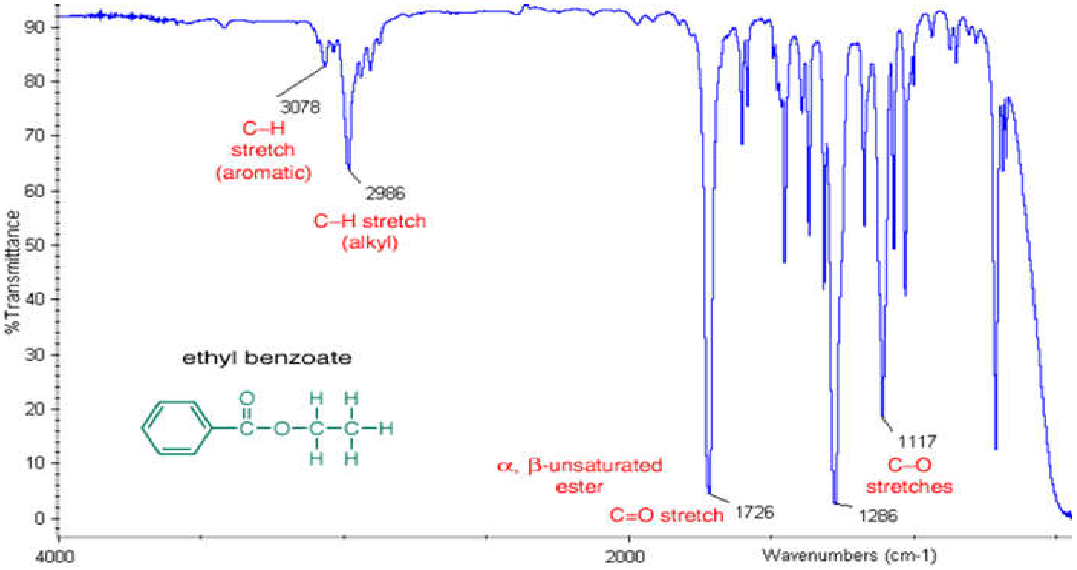


Fig. 25: IR spectra of Ethylbenzoate

Amides

1. Amides show the bands similar to those of amines.
2. In addition, they show a carbonyl band at 1710–1610 cm^{-1}(called amide I-band, Figure 26) and another (called amide II-band) at frequency slightly lower (1670-1640 cm^{-1}) than the carbonyl band for example Acetamide CH_3CONH_2 has amide I-band at 1650 cm^{-1} and amide II band at 1635 cm^{-1} [14-19].
3. The N – H stretching band at 3350, 3175 & 2970 cm^{-1}.

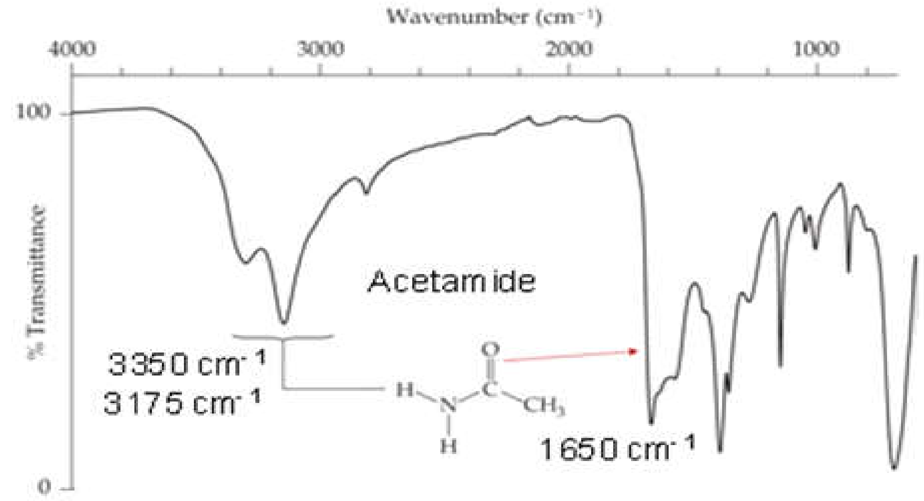


Fig. 26: IR spectra of Acetamide

Acid Anhydrides

1. They are distinguished from other acid derivatives by the appearance of two C=O bands. The two C=O stretching frequencies (asymmetric and symmetric) occurring near 1825, 1760 cm^{-1} respectively with a separation of about 60 cm^{-1}.
2. The higher frequency band in general is more intense in open chain anhydride while the lower band is more intense in case of strained cyclic (three, four and five member) anhydrides.
3. Strong bands appear in the spectrum of anhydrides near 1300-900 cm^{-1}due to C-O stretching vibrations. Non conjugated open chain anhydrides (except acetic anhydride 1125 cm^{-1}) exhibit strong band near 1050-1030 cm^{-1} whereas cyclic anhydrides display bands near 950-900 and 1300-1150 cm^{-1} (Figure 27).

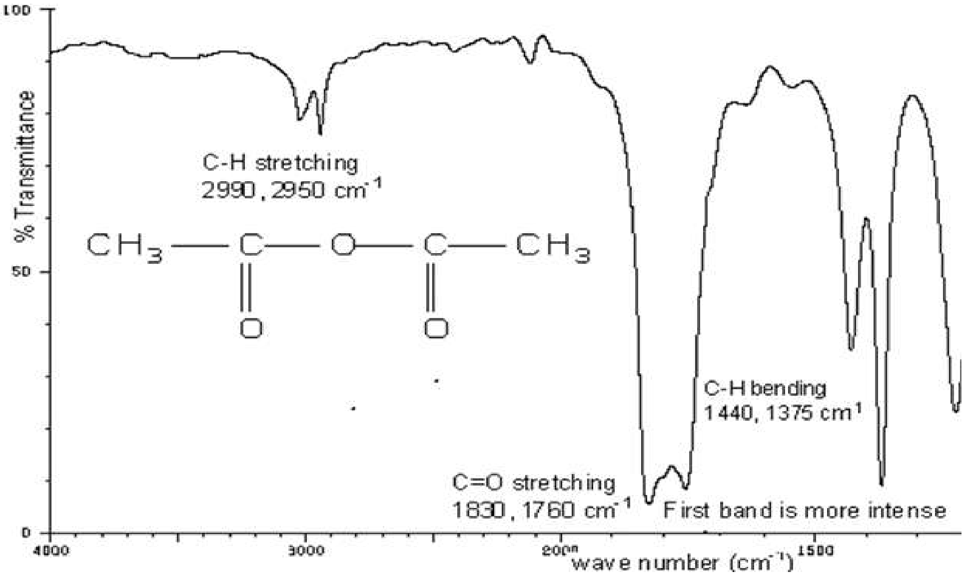
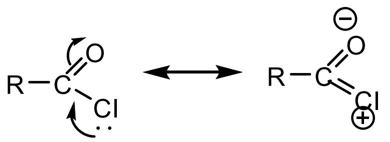


Fig. 27: IR spectra of acetic anhydride.

Acid Halides

1. The appearance of strong C=O stretching absorption in the range of 1870-1770 cm^{-1} is main characteristic of acid halides.
2. Acid chlorides, the most common acid halides exhibits bands for C=O around 1800 cm^{-1} (Figure 28). The high absorption band for C=O in acid chlorides is attributed to electronegativity of chlorine which makes it hard for oxygen to withdraw electrons from carbonyl carbon and hence weakens resonance (Scheme 8).



Scheme 8: Resonance in acidchloride.

3. Conjugated acid halides absorbs at slightly lower frequency band for C=O.
4. In aromatic acid chlorides a strong shoulder usually appears lower side of the C=O band. This occurs due to Fermi resonance between the C=O stretching band and first overtone of the band near 875 cm^{-1} (Figure 29).

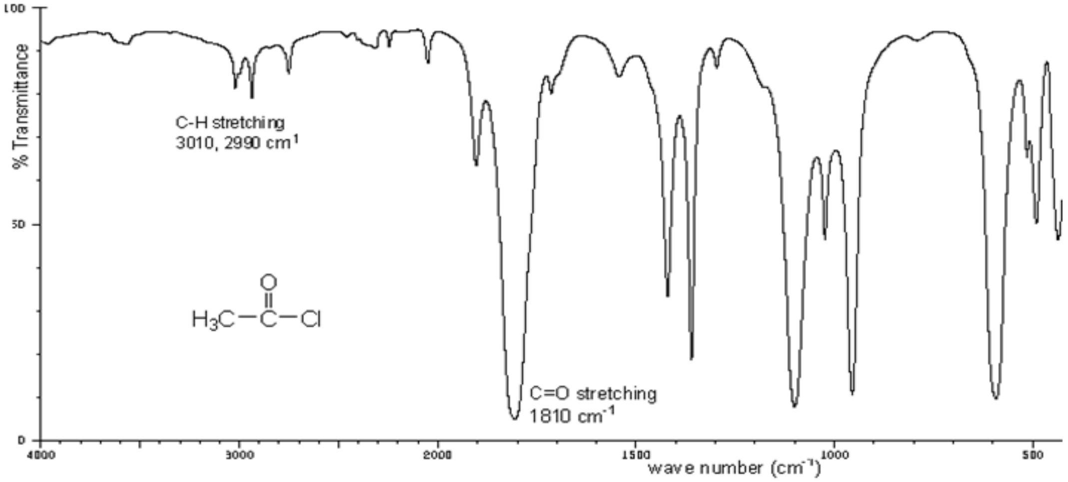


Fig. 28: IR spectra of Acetylchloride.

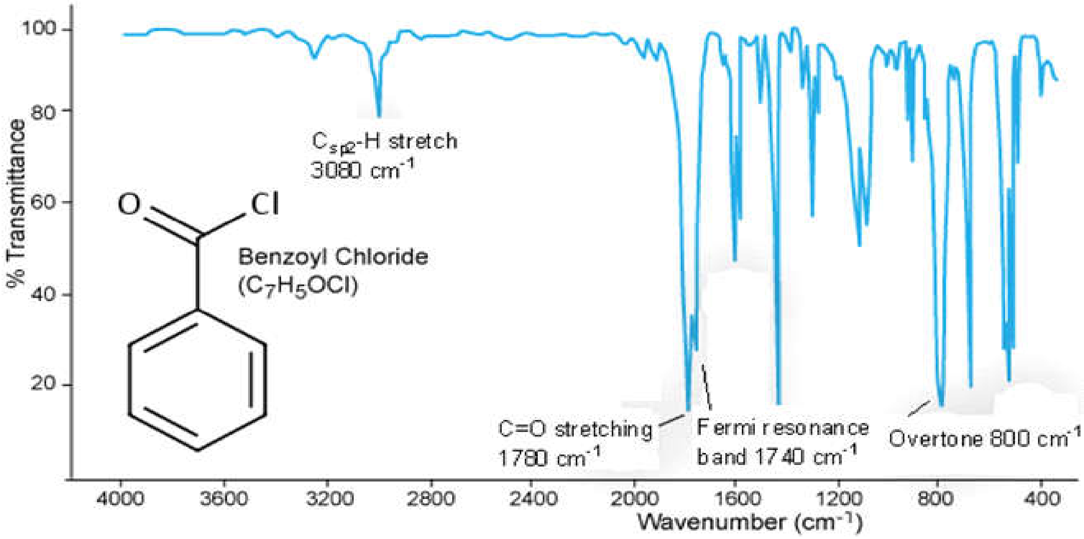


Fig. 29: IR spectra of Benzoylchloride

Amines

1. Primary and secondary amines show the N–H stretching bands at 3500-3300 cm^{-1} and N–H deformation bands at 1650–1500 cm^{-1} (Figures 30, 31).
2. Tertiary amines have no N-H stretching vibrations (Figure 32), however detected indirectly. The tertiary amine is converted into the amine salt (say $R_3N^+HCl^-$) and this salt shows a strong ammonium band in the range 3000–2200 cm^{-1}.
3. Aromatic amines (aniline) are further characterized by bands at 1350–1250 cm^{-1} and 1280-1180 cm^{-1}.
4. N-CH_3 stretching bands at 2850–2750 cm^{-1} sometimes characterize methylamines (N-methyl aniline and N, N-dimethyl aniline).

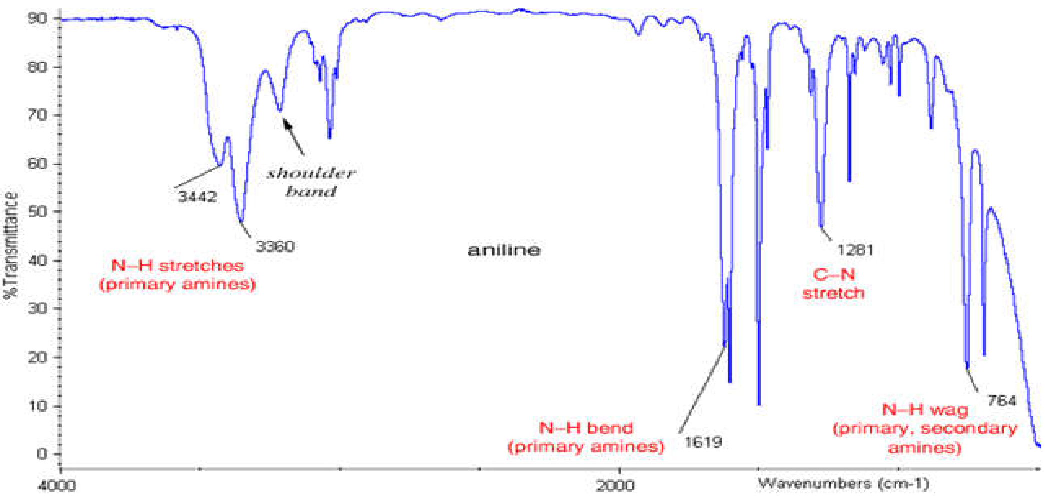


Fig. 30: IR spectra of Aniline

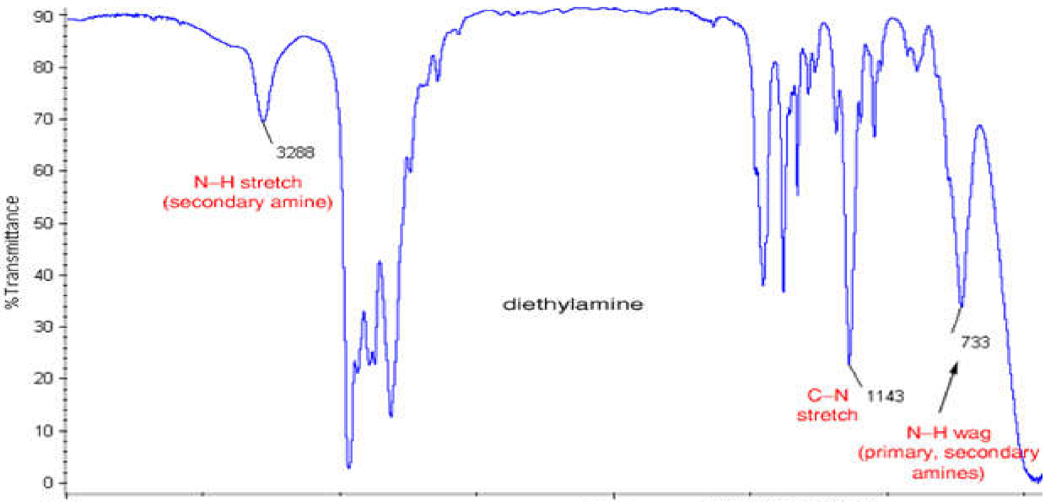


Fig. 31: IR spectra of Diethylamine

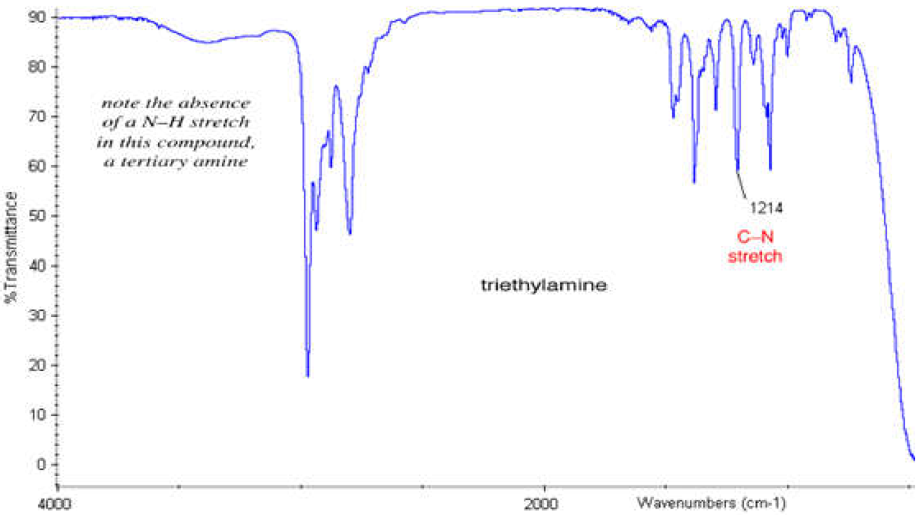
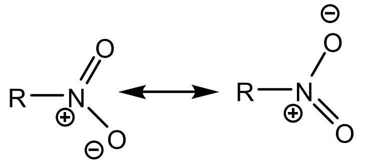


Fig. 32: IR spectra of N,N,N-Triethylamine

Nitro Compounds

1. The nitro group has two similar N-O bonds which yield asymmetrical stretching band in 1565-1515 cm^{-1} and symmetrical stretching band in 1385-1335 cm^{-1}. This is due to highly polar nitrogen –oxygen bond, Scheme 9.



Scheme 9: Resonance in alkylnitrate

2. In aliphatic compounds bands appear slightly at higher frequency (1550-1380 cm^{-1}) than in aromatic compounds (1530-1350 cm^{-1}) (Figure 33). This is due to conjugation of nitro group with aromatic ring.
3. In aromatic nitro compounds, if there is electron releasing group at ortho or para-position with respect to nitro group NO_2 stretching frequency considerably decreases, because of resonance which weakens N-O bond. Conversely electron pulling group enhances the frequency band.

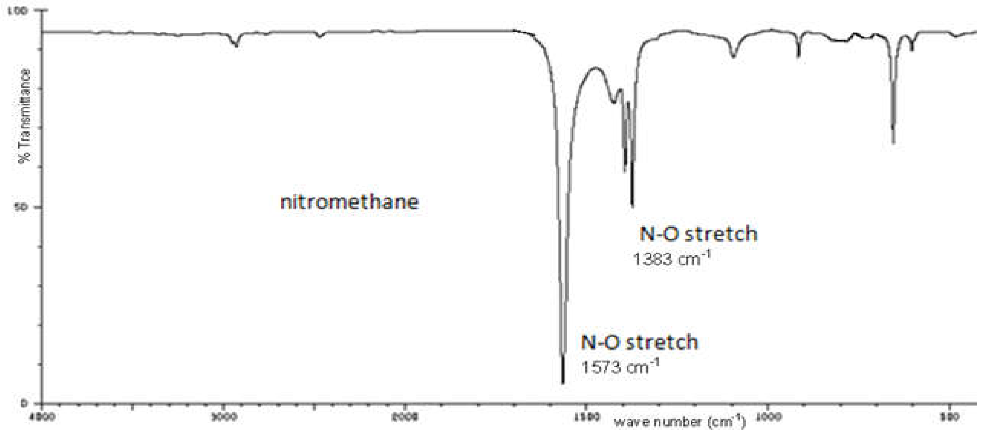


Fig. 33: IR spectra of Nitromethane.

2. Fingerprint Regions in an IR Spectrum

The region 1300-900 cm^{-1}, known as the fingerprint region, of an IR spectrum is characteristic of a molecule as a whole (Figure 34). No two compounds, howsoever closely related, can have identical or super imposable bands in this region. The finger print region of an IR spectrum is thus very useful for establishing the identity of two compounds. In fact, the superimposability of the IR spectra of two compounds is taken as an unimpeachable evidence for the identity of the two compounds.

If the identify of two solid, crystalline compounds is to be established, they must be crystalline under exactly identical conditions before their IR spectra are taken for the purpose.

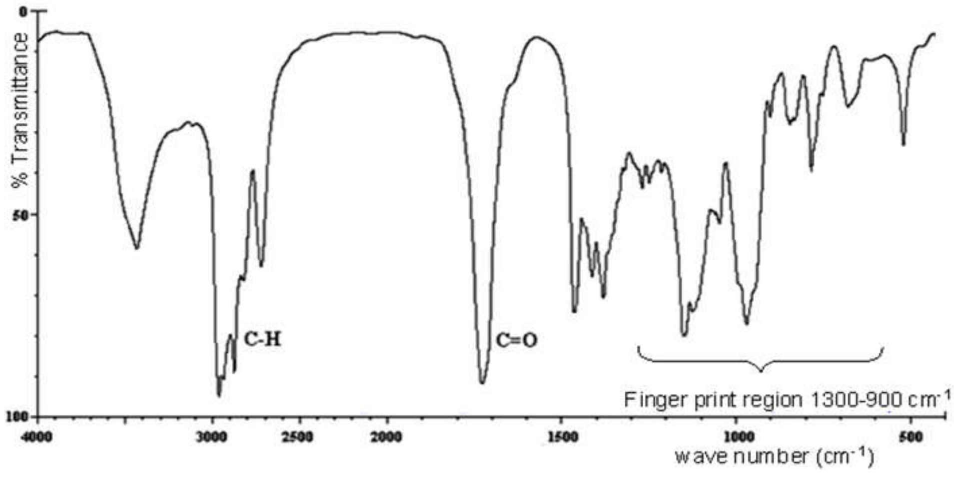


Fig. 34: Fingerprint region of IR spectra.

3. *Aromatic Region (Aromatic hydrocarbons)*

1. At least one strong band between 900 and 650 cm^{-1} is the typical aromatic band.
2. In addition the C = C stretching band at 1600 – 1575 cm^{-1} usually appears as a duplet.
3. The C–H stretching band corresponding to unsaturated hydrocarbons appears at 3100-3000 cm^{-1}
4. There are diagnostic pattern of weak bands between 2000-1650 cm^{-1} for substituted benzene ring. For example.

Mono substituted	Distinct 'fingers', the strongest at 2000 cm^{-1} (Figure 35).
Ortho Substituted	Two triplet bands
Meta Substituted	Two bands and a triplet around 1650 cm^{-1}
Para Substituted	Two bands, the stronger one around 2000 cm^{-1}

5. There are additional characteristic band between 700-850 cm^{-1} for substituted benzene rings. For example.

Mono substituted	770-700 cm^{-1} and 700-680 cm^{-1}
Ortho Substituted	770-735 cm^{-1} (Figure 36).
Meta Substituted	800-750 cm^{-1} and 700-680 cm^{-1} (Figure 37).
Para Substituted	800-850 cm^{-1} (Figure 38).

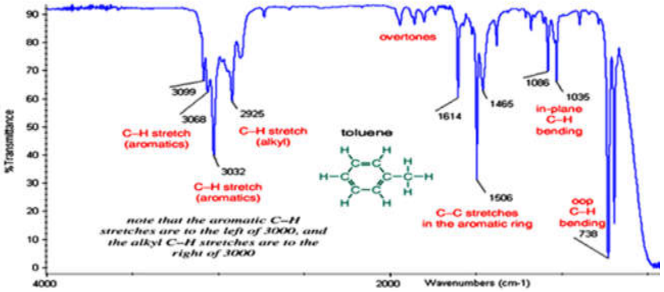


Fig. 35: IR spectra of Toluene

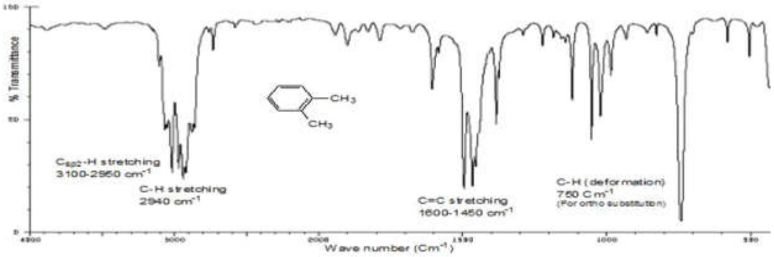


Fig. 36: IR spectra of ortho- xylene

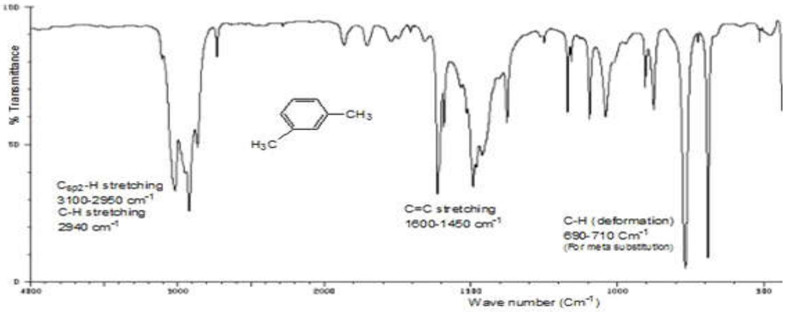


Fig. 37: IR spectra of meta- xylene

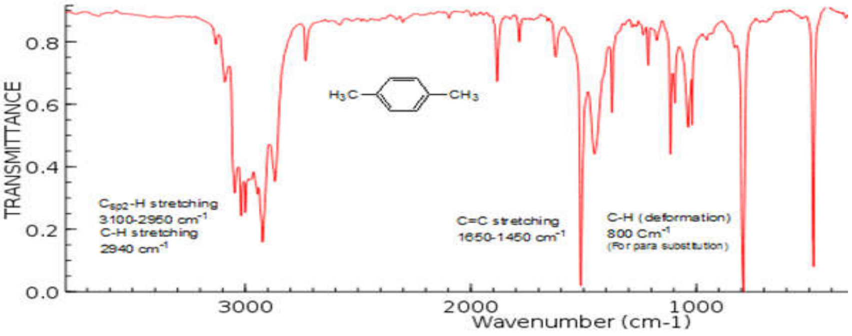


Fig. 38: IR spectra of para- xylene

Simplest Approach for interpreting IR spectrum

1. Is a carbonyl group present?

   The C=O group gives rise to a strong absorption in the region 1820-1660 cm $^{-1}$. The peak is often the strongest in the spectrum and of medium width. You can't miss it.

2. If C=O is present, check the following types (if absent, go to 3).

ACIDS	Is OH also present? Broad absorption near 3400-2400 cm -1 (usually overlapped C-H stretching) is obtained
AMIDES	Is NH also present? Medium absorption near 3500 cm-1 sometimes a double peak, with equivalent halves is observed.
ESTERS	Is C-O also present? Strong intensity absorptions near 1300-1000 cm-1 is apparent.
ANHYDRIDES	have two C=O absorptions near 1810 and 1760 cm-1
ALDEHYDES	Two weak absorptions near 2850 and 2750 cm-1 on the right hand side of CH absorption appears.
KETONES	The above 5 choices have been eliminated

3. If C=O is absent

ALCOHOLS	Check for OH (broad absorption near 3600-3300 cm-1) Confirm this by finding C-O near 1300-1000 cm-1
AMINES	Check for NH (medium absorption (s) near 3500 cm-1)
ETHERS	Check for C-O near 1300-1000 cm-1 and absence of O-H

4. *Double Bonds and / or Aromatic Rings*

   C=C is a weak absorption near 1650cm^{-1} medium to strong absorptions in the region 1650-1450 cm^{-1} often imply

   For an aromatic ring, confirm the above by consulting the CH region; aromatic and vinyl CH occurs to the left of 3000 cm^{-1} (aliphatic CH occurs to the right of this value)

5. *Triple Bonds*

   Ca”N is a medium, sharp absorption near 2250 cm^{-1}

   Ca”C is a weak but sharp absorption near 2150 cm^{-1}

   Also check for acetylenic CH near 3300 cm^{-1}

6. *Nitro groups*

   Two strong absorptions in 1600-1500 cm^{-1} and 1390-1300 cm^{-1} region.

7. *Hydrocarbons*

   None of the above is found, major absorptions are in CH region near 3000 cm^{-1}. Simple spectrum, other absorptions are only near 1450 cm^{-1} and 1375 cm^{-1}.

Fourier Transform Infra red Spectroscopy (FTIR)

- In Conventional or dispersive IR polychromatic or grating will be employed for dispersing the polychromatic radiation.
- The energy of individual frequent is scanned sequentially.
- For good quality spectra (resolution) narrow shuts are required.
- In FTIR an interferometer is employed instead of a grating or prism.
- The spectral information for all the frequencies is obtained at the same time.
- The most common interferometer used is Michelson interferometer (1891).
- of functional groups
- Striation elucidate Identification of compounds
- Analysis on
- Retention of intra – and intermolecular interaction convent technique
- Non – destructive
- Rapid and simple
- Gases, liquids and solids can be examined
- Various sampling Techniques

Main Features of Dispersive and FTIR

- In Conventional or dispersive IR polychromatic or grating will be employed for dispersing the polychromatic radiation.
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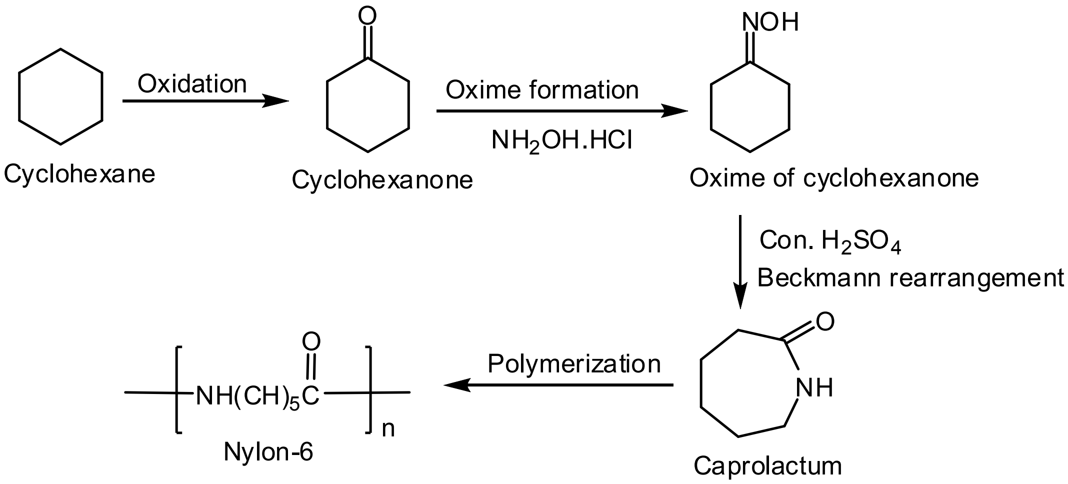
- In FTIR an interferometer is employed instead of a grating or prism.
- The spectral information for all the frequencies is obtained at the same time.
- The most common interferometer used is Michelson interferometer (1891).

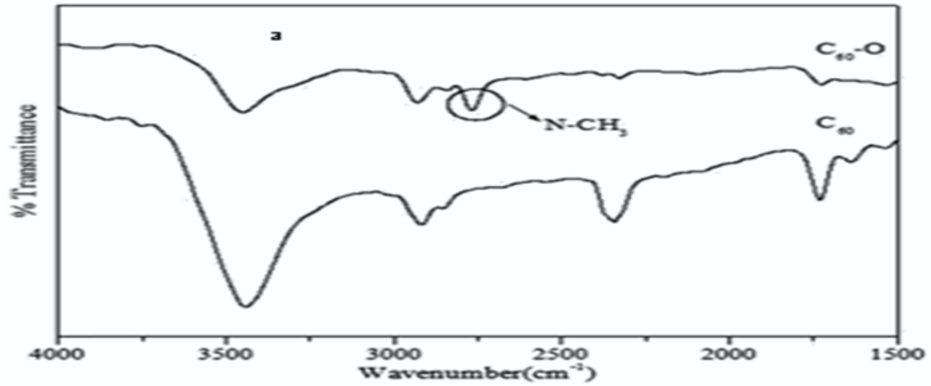
Applications of FTIR

The FTIR microscopes makes almost any type of sample that would be analyzed by FTIR more easily examined on a micro scale. The different applications are described below:

Polymers are ubiquitous in our society, and their prevalence at crime scene causes them to be commonly encountered as forensic evidence. The large variety of polymer types makes it necessary to categorize them by application in order to gain a general understanding of variations within each group. Thus classified, the evidence may often be individualized to a greater extent, its significance more clearly understood, and its evidentiary value enhanced. The forensic examination of fibers by visual light microscopy is complemented by FTIR microscopy. FTIR plays an important role in the systematic approach to the complete characterization of fibers. FTIR data will provide an unequivocal of the generic class, as well as the subclass created by chemical variations within the generic class. In addition, the American society of testing and Materials (ASTM) now lists FTIR spectroscopy as the preferred method of analysis for identifying man-made fibers, stating, " where the data are consistent and the spectra obtained and interpreted by an experienced spectroscopist, the FTIR procedure has no known bias". The IR spectra of nylon-6 fibers (method of synthesis given in scheme 10, below) obtained by different methods are given in figure 39 a-d, below:



Scheme 10: Synthetic route of nylon-6



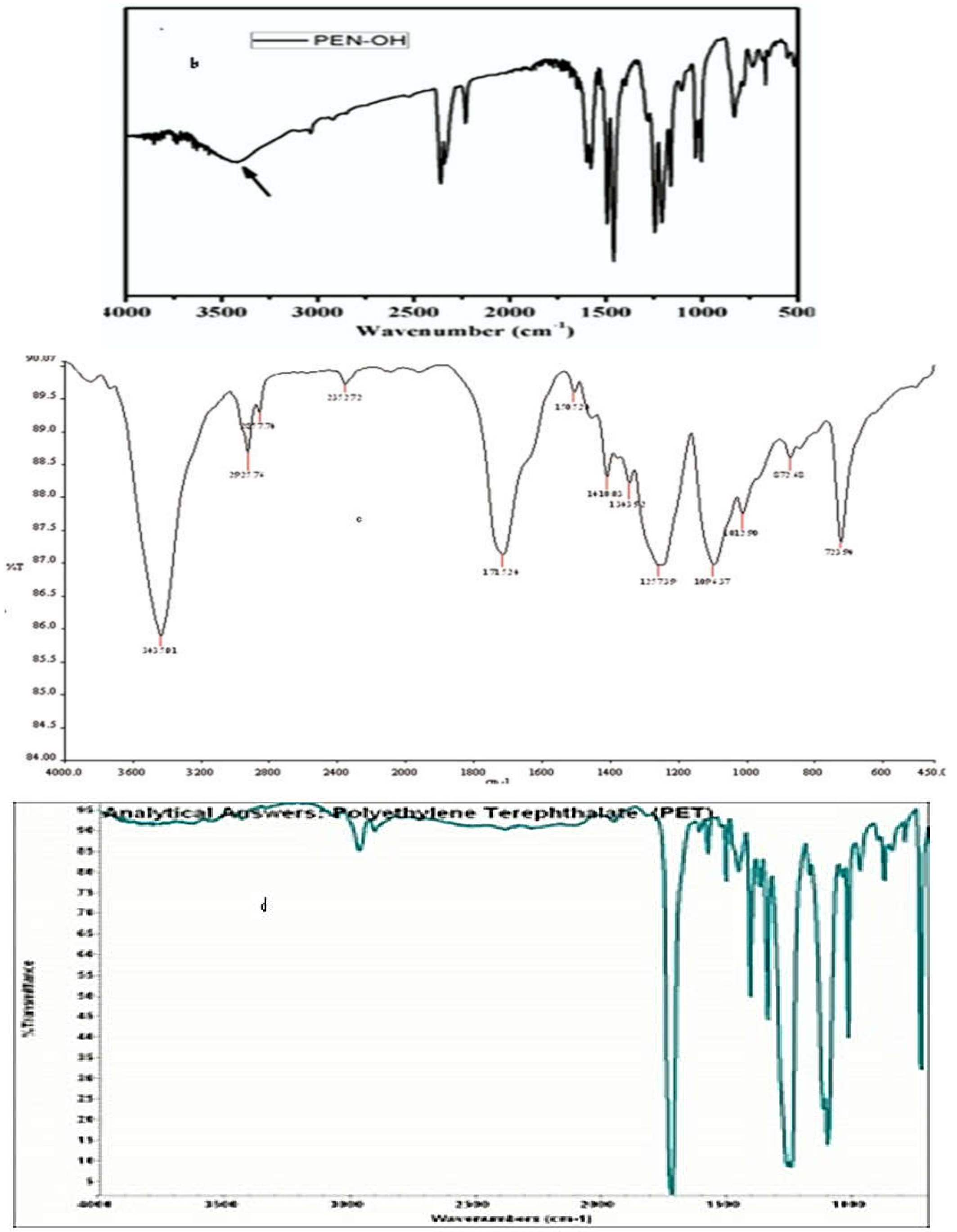


Fig. 39: **(a)** Spectrum of nylon-6 obtained by lead foil technique on a dispersive instrument, **(b)** Spectrum of nylon-6 fibers obtained by diamond cell on a dispersive instrument, **(c)** spectrum of nylon-6 fibers obtained by diamond cell on FTIR, **(d)** spectrum of fortrel fibers obtained by diamond cell on FTIR. A comparison of spectras a-c explains the effect of different sampling techniques and different instrument types

The ingredients and residues associated with various explosive devices are comprised of a wide variety of different substances, including organic compounds, inorganic salts, and polymers. The wide variety makes FTIR an ideal tool, not for screening such substances, but also for identification in most systematic approach. The two strong absorption bands of symmetric and asymmetric stretching vibrations of the NO_2 group in nitro explosives depend on the type of atoms with which it is directly attached. These vibrations have an important investigative value and their presence and absence in the sample should be the first thing to be noticed. In the spectrum of 2,4,6-trinitrotoluene (Figure 40) the two C-NO_2 asymmetric and symmetric stretching bands appear at 1534 cm^{-1} and 1354 cm^{-1}.

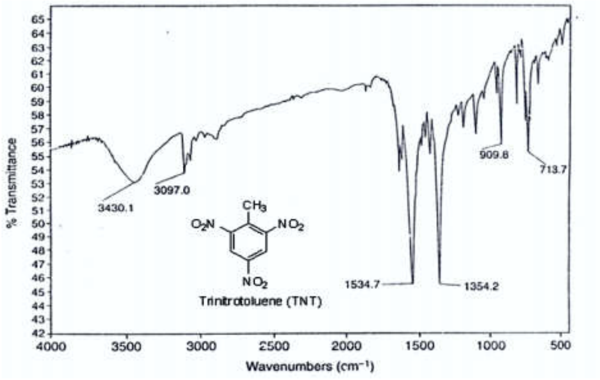


Fig. 40: IR spectrum of Trinitrotoluene (TNT)

The nitrate esters, C-O-NO_2 have two strong asymmetric and symmetric stretching vibrations in the range 1660-1640 cm^{-1} and 1285-1270 cm^{-1} respectively.

It is found that these bands in polynitrate ester explosives split into two or more peaks which is attributed to the existence of rotational isomers, due to hindered rotation around C-C bond. Figures 41-45; spectra of pentaerythritol tetranitrate, ethylene glycol dinitrate, nitroglycerine, nitrocellulose and metriol trinitrate respectively prove this finding.

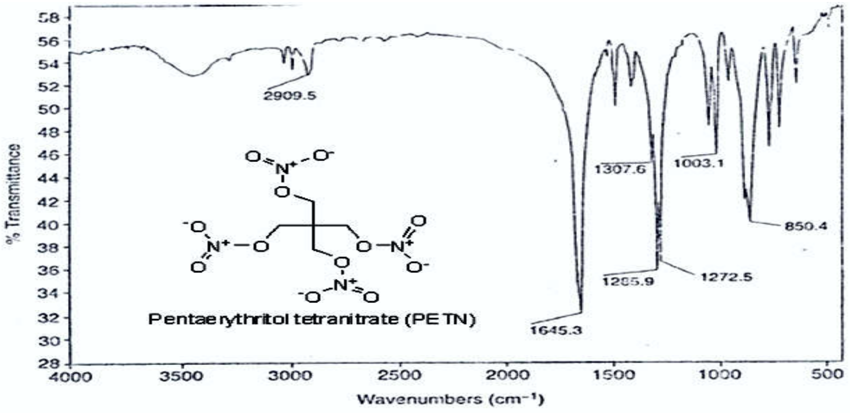


Fig. 41: IR spectrum of pentaerythritol tetranitrate

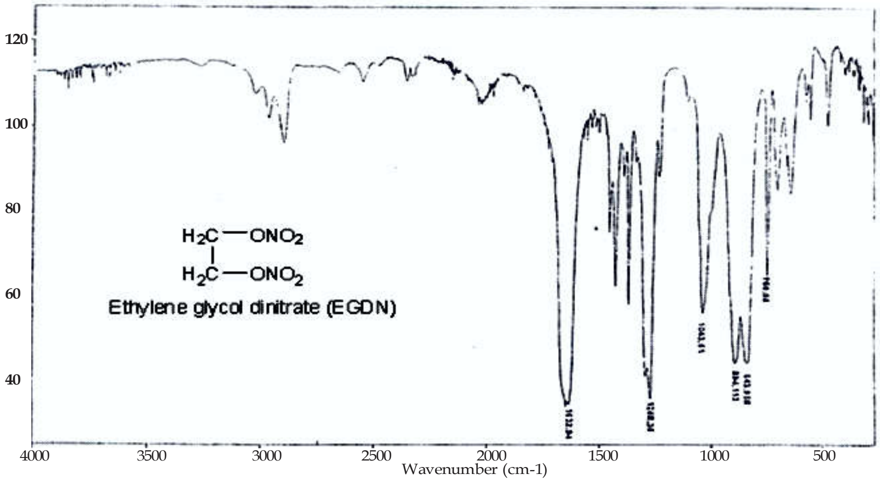


Fig. 42: IR spectra of ethyleneglycol dinitrate

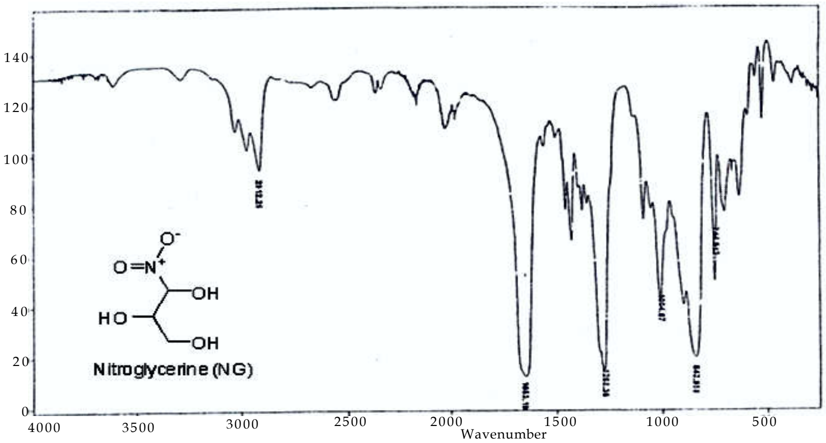


Fig. 43: IR spectra of nitroglycerine

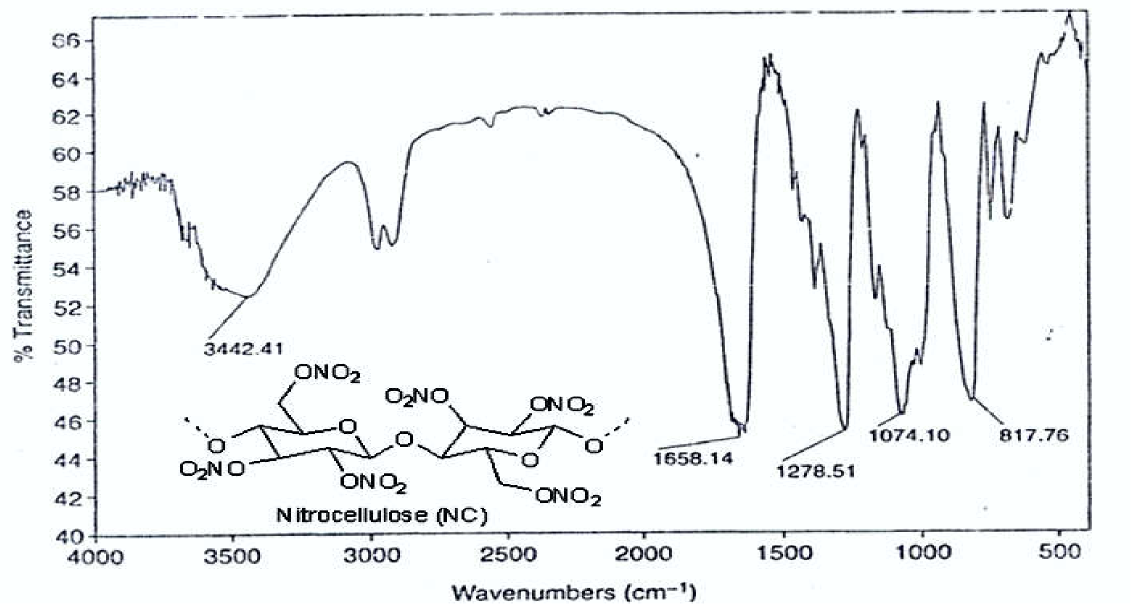


Fig. 44: IR spectra of nitrocellulose

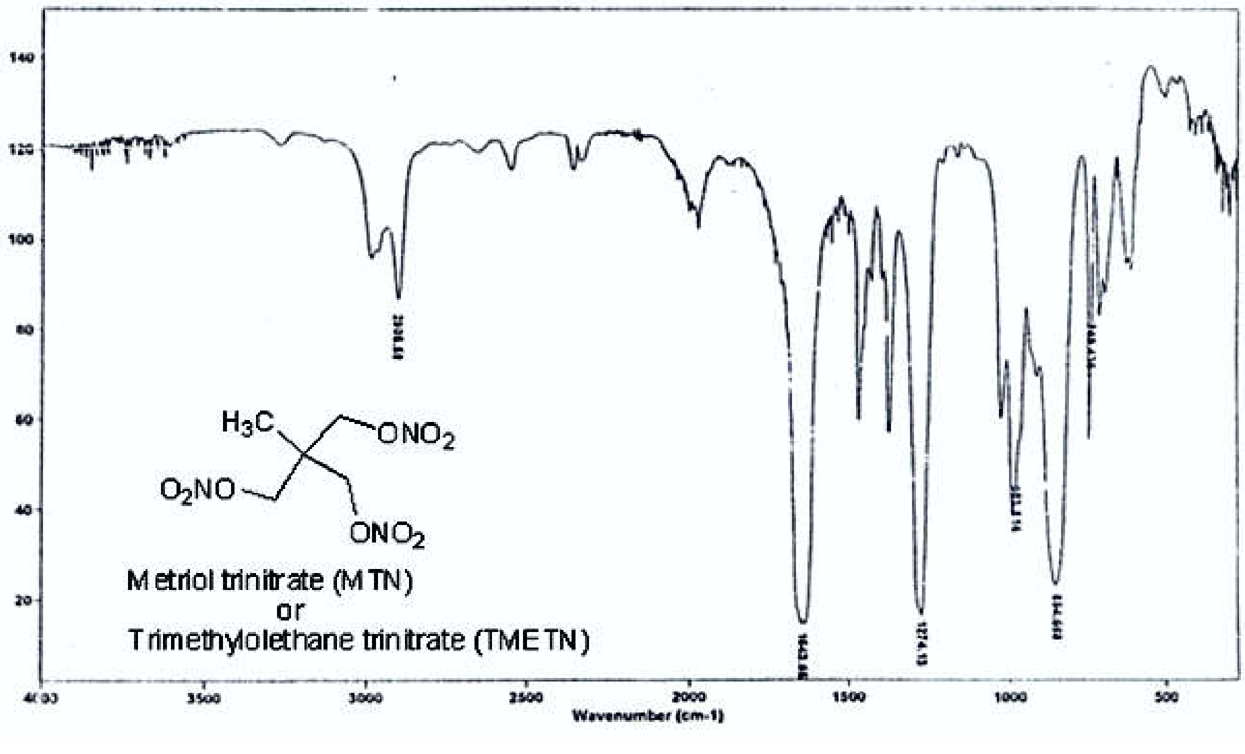


Fig. 45: IR spectra of metriol trinitrate

In nitramine explosives two NO stretching vibrations of the N-NO_2 bond were reported in the range 1590-1530 cm^{-1} and 1310-1270 cm^{-1} for asymmetric and symmetric stretching vibrations respectively. Figures 46 and 47 show the IR spectra of heterocyclic nitramines RDX (tricyclomethylene trinitramine) and HMX (tetracyclomethylene tetranitramine) in which various peaks appear listed in the above region.

The powerful organic peroxide explosives are usually unstable and sensitive to heat, friction and shock, hence they are not considered as primary standard explosives. The band at 872 cm^{-1} was attributed to O-O stretching vibrations in peroxides. The IR spectra of hexamethylene triperoxide diamine is given in Figure 48 [20].

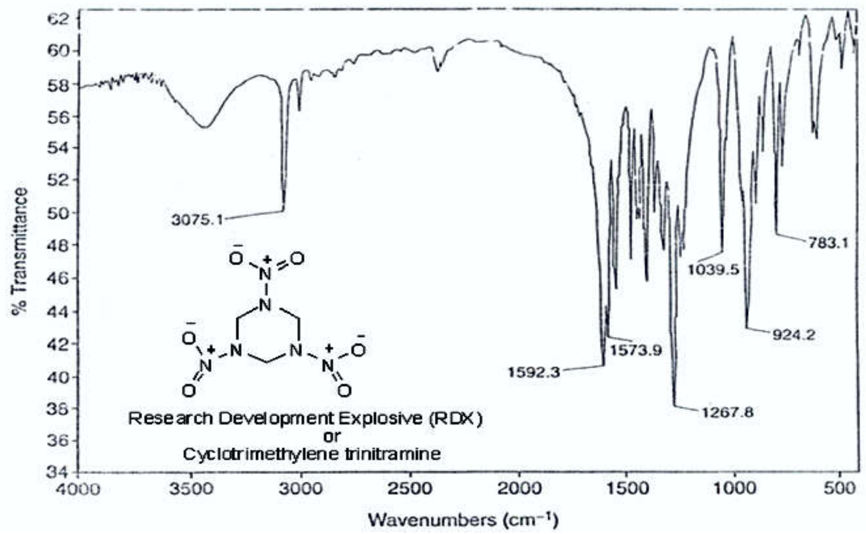


Fig. 46: IR spectrum of RDX

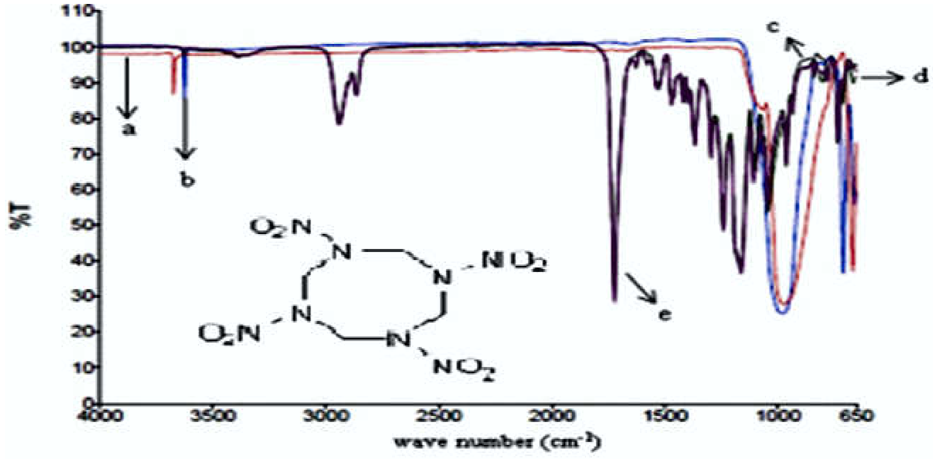


Fig. 47: IR spectrum of HMX

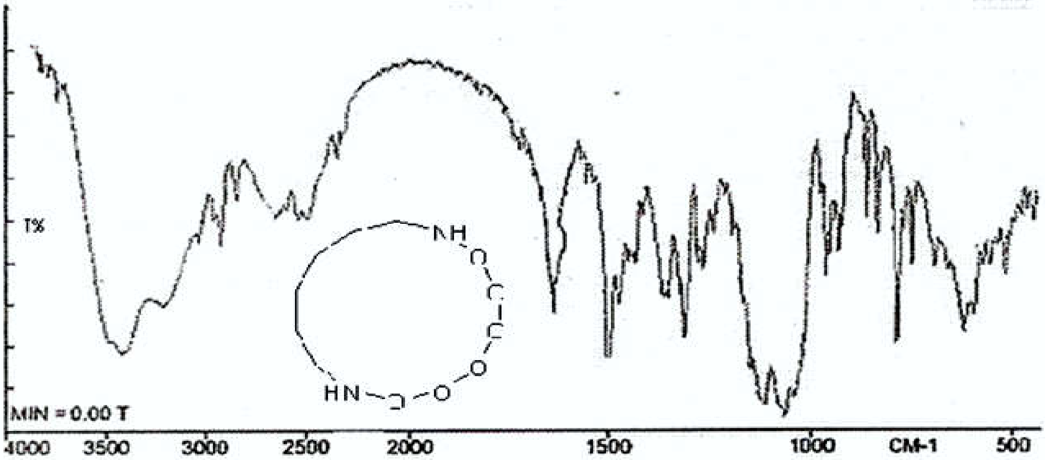


Fig. 48: IR spectrum of hexamethylene triperoxide diamine

Inorganic anions emerge as oxidants in explosive mixtures. Nitrates are important commercial explosives and mixed in black powders namely, dynamite slurries, emulsions and ammonium nitrate-fuel oil (ANFO). The common nitrates salts used in explosives are ammonium (NH_4NO_3) (Figure 50), sodium ($NaNO_3$) and potassium (KNO_3) (Figure 49). Ammonium nitrate is most common and has been identified in many terrorist bombings. Chlorates (ClO_3^-) (Figure 51) have usually been avoided in commercial explosives, being very unpredictably dangerous. The appearance of these anions is characterized by IR bands in respective regions viz; nitrates (1380-1350 cm^{-1}; very strong, 840-815 cm^{-1}; medium), chlorates (98-940 cm^{-1}; very strong), sulphates (1130-1080 cm^{-1}; very strong, 680-610 cm^{-1} medium weak), carbonates (1450-1410 cm^{-1}; very strong, 880-810 cm^{-1}; medium). The IR spectra of potassium nitrate, ammonium nitrate, sodium chlorate, potassium chlorate, potassium perchlorate and potassium sulphate are depicted below (Figure 52-54):

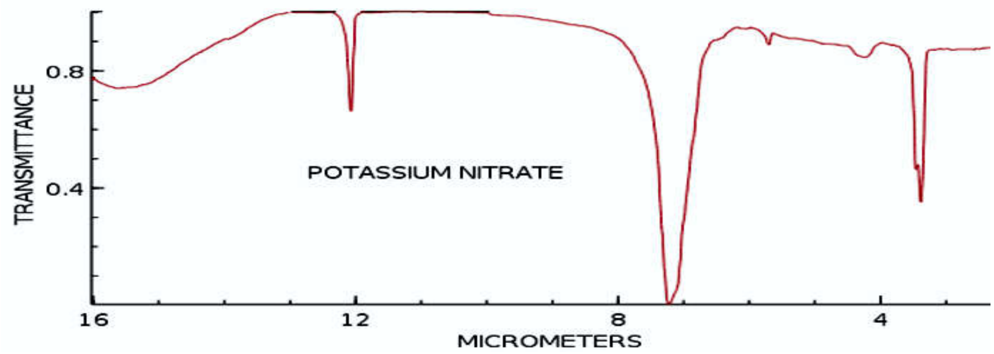


Fig. 49: IR spectrum of potassium nitrate (KNO_3)

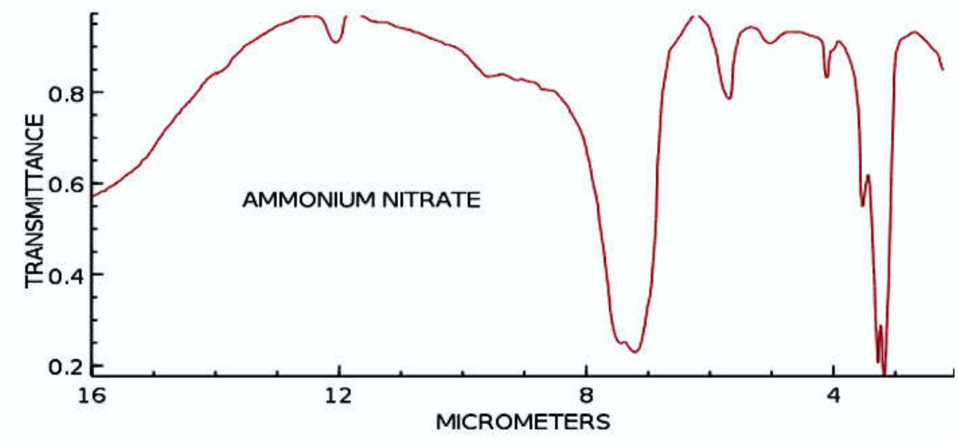


Fig. 50: IR spectrum of ammonium nitrate (NH_4NO_3)

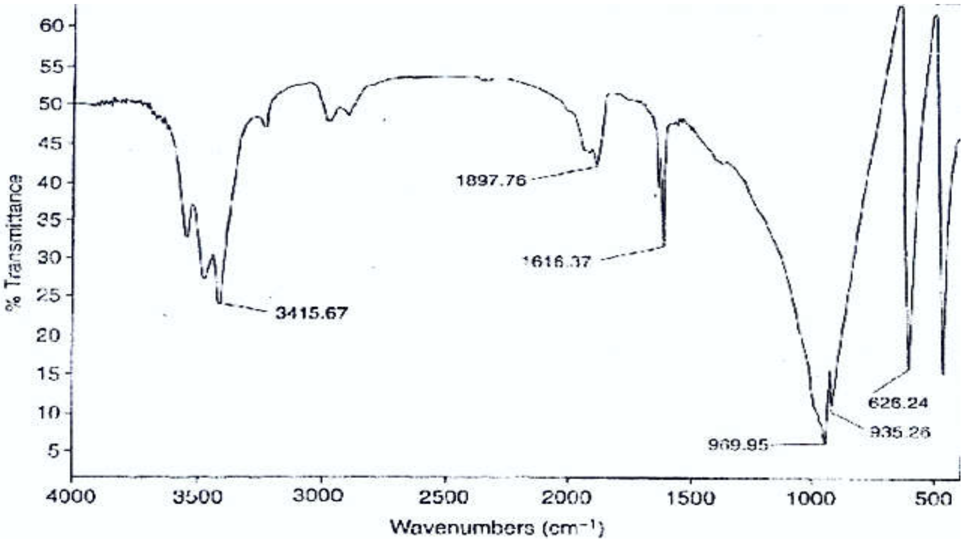


Fig. 51: IR spectrum of sodium chlorate

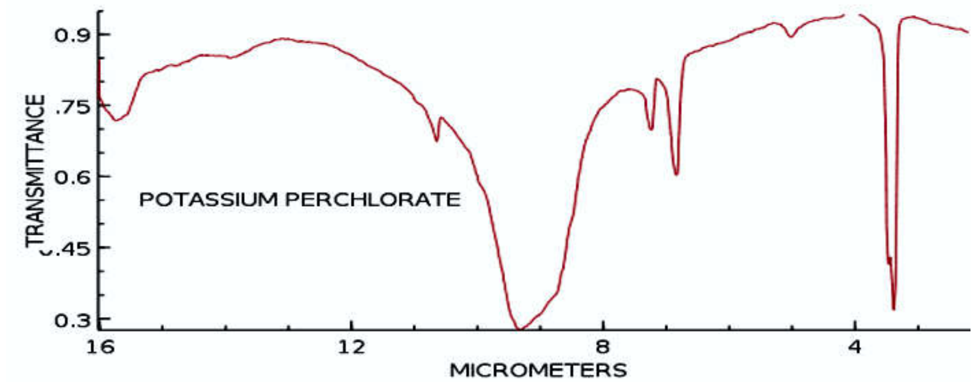


Fig. 52: IR spectrum of potassium chlorate ($KClO_3$)

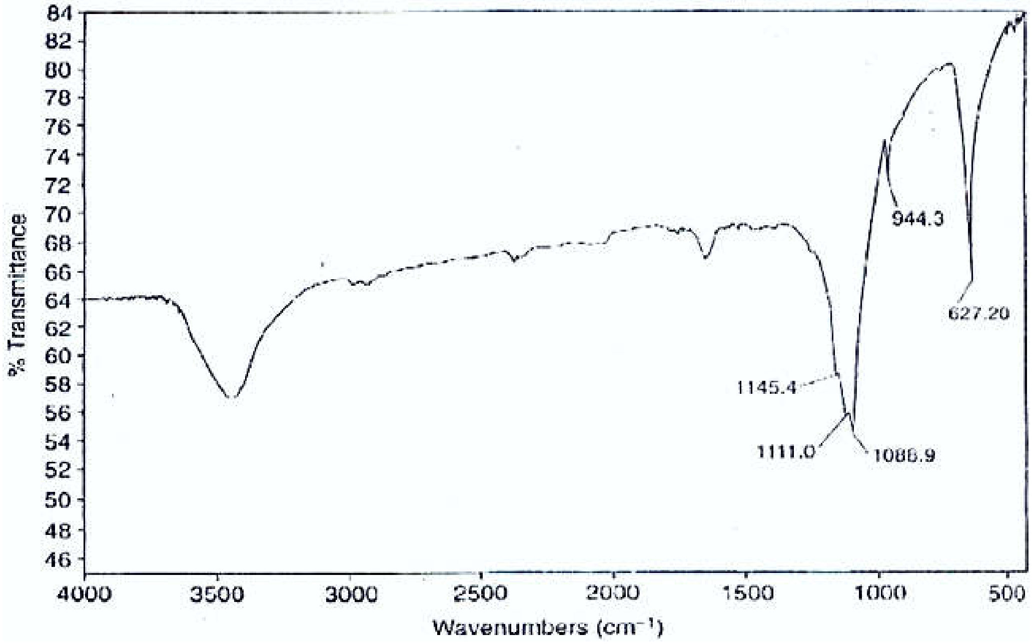


Fig. 53: IR spectrum of potassium perchlorate ($KClO_4$)

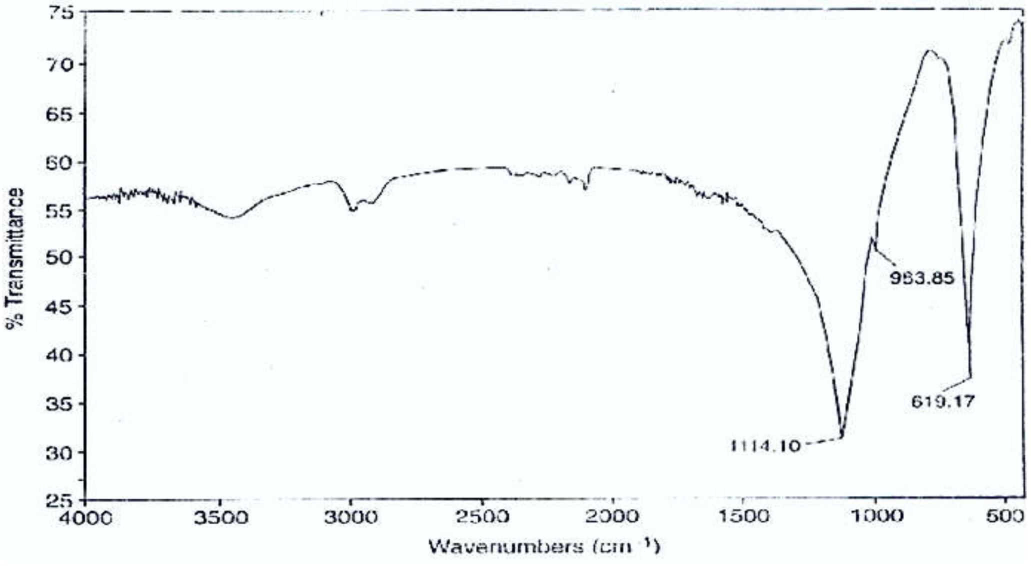


Fig. 54: IR spectrum of potassium sulphate (K_2SO_4)

Automobile producers currently place a great deal of emphasis on polymeric components. The need for lightweight, non-corrosive part has become important. Plastic parts are found throughout automobiles in including the outer bodies. Although there has not been extensive reporting of the analysis of these components using FTIR microscopes, a few papers have appeared.

Adhesives and tapes are frequently removed at crime scenes from explosive devices, bound victims, etc. Bartick and Merrill have reported the application of FTIR for the analysis of black plastic tapes. Both the adhesive and backing were sampled with a standard-size FTIR accessory. This approach works well unless the tape is contaminated and it is difficult to find a clean portion. Contamination of the adhesive poses the most concern because it is more difficult to clean. One advantage of FTIR is that small areas may be isolated within a particular specimen, thus eliminating tedious separation procedures. Additional polymers are frequently found at crime scenes and can often be useful as physical evidence. These are frequently analyzed by FTIR. The ease of preparing samples and recording spectra with FTIR has resulted in the method becoming widespread, not only for micro samples but also for samples that would normally be considered on a microscopic scale. Several methods of sampling inks have been reported which vary for the type of ink and the substrate. FTIR spectra of inks removed from printed paper by scraping inks from graph paper have been reported. The ability to directly obtain FTIR spectra of writing inks on documents with a microscope is difficult because of the absorption of the substrate, typically paper. FTIR is very useful tool for the analysis of many inorganic substances. The acquisition of mineral spectra by both transmission and reflection spectroscopy have been developed. Dentine and enamel from human teeth, calcium phosphates, were compared by reflectance with an FTIR microscope. Another example of mineral analysis was the comparison of several metamorphic phases of single rock.

These can contribute to FTIR spectra and interfere with the interpretation of the data. One must be particularly careful with micro sampling, because the relative contaminants contributions can be significantly greater then routine size samples. For example the presence of a contaminant can also, however, increase the evidential value of a fiber match when the contaminant is shown to be present on both the questioned and known samples. Common binders for water base architectural coatings (house paints) include poly (vinyl acetate) acrylic, PVA acrylic, styrene acrylic, and styrene-butadiene are often used in oil base paints. Like automotive undercoats, house paints may contain a variety of different pigments and extenders. As in the case of automotive undercoats, differences in the types and relative amounts of these pigments serve to differentiate among house paints, and their spectra likewise exhibit considerable diversity.

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Case Report

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Suicidal Cut Injury of Wrist: Crime Scene and Autopsy Findings

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Abstract

Cut Injury of wrist (CIW) is also known as 'Spaghetti wrists' with a minimum of three completely transected structures, a nerve, artery and a tendon. The investigators have to answer the most challenging question i.e. manner of death. Some circumstances cannot be understood by the investigators and have to be explained by a Forensic Pathologist. We report a case of an individual who was found dead in a bathroom with blood splashes all over the walls and floor of the bathroom along clothes and body of the deceased. The amount of blood found in the bathroom was baffling. The case later examined in totality with autopsy findings was found to be suicidal in nature. The authors intend to recommend that wherever possible the autopsy surgeon should visit the crime scene in such cases before conducting autopsy to have a fair idea about the circumstances of death and to lead the investigation towards natural course of justice.

Keywords: Cut Injury of Wrist; Spaghetti Wrists; Ulnar Artery; Hypovolemic Shock; Suicide.

Introduction

In a case of violent death by Cut Injury of Wrist (CIW) , the question of deciding the manner of death always pose a challenge to the Investigators and Autopsy Surgeons. A combined approach has to be taken by considering the crime scene and circumstantial evidences together with the autopsy findings. Police officer in India being a non Medical person can sometimes get confused by the findings at a crime scene, so it is the responsibility of the autopsy surgeon to clarify the doubts of investigator. We report a case of an individual who was found dead in a bathroom with blood splashes walls and floor of the bathroom along clothes and body of the deceased. The case later examined in totality with autopsy findings was found to be suicidal in nature. The authors intend to add to Medical Literature the autopsy findings and type of crime scene which can be found in cases of suicide by cutting of wrist.

Case History

The deceased was found unresponsive in the bathroom of his Hotel room in New Delhi which was locked from inside and was broke open by the hotel staff. A blade piece was found nearby. The deceased was brought to the AIIMS casualty and declared brought dead.

Autopsy Findings

The deceased was of stout built with height 5'8" inch. Blood stains were present on both forearms, hands, chest, trunk and legs. He was wearing blood soaked green half sleeved T-shirt, blood soaked green Bermuda shorts and blood soaked underwear. Rigor mortis was present over eyes, jaw, trunk, upper limbs. Postmortem lividity was pale and present over back and dependant areas except pressure areas.

The following external injuries were present:

1. Multiple parallel skin deep linear incised wounds varying in length from 6 cm to 8 cm are present over the dorsal aspect of left forearm. The wounds were placed horizontal to the long axis of the forearm and tailing is present near the radial side of the forearm. The margins of the wounds were clean cut, regular and blood stained.
2. A wound of size 6x3 cm was present on the inner aspect of the left wrist region cutting through the skin, subcutaneous tissue, flexor tendons, Ulnar artery, Ulnar nerve. The wound was placed horizontally to the long axis of the wrist with clean cut and regular margins.
3. Three parallel skin deep linear incised wounds varying in length from 5 cm to 8 cm were present over the medial aspect of the left leg just proximal to the medial malleolus. The wounds were placed horizontal to the long axis of the leg and tailing was present near the medial side of the leg. The margin of the wound was clean cut, regular and blood stained.

Image 1: Crime Scene Photograph

Image 2: Crime Scene Photograph

Image 3: Crime Scene Photograph

Image 4: Crime Scene Photograph

The Internal organs were pale. Stomach contained about 100 ml of blackish colored fluid and mucosa was congested. Viscera was preserved for chemical analysis to rule out any concomitant intoxication and came negative for any common poisons tested in the Forensic Science Laboratory. The cause of death was opined as Shock due to hemorrhage consequent upon antemortem cut injury of the wrist caused by sharp object.

Discussion

Suicidal wounds by knife are commonly found in men over throat, neck and front of chest, typically multiple and are associated with a number of Hesitation/ Tentative cuts. In wrist cuts, due to right handedness the usual site is the left wrist on the flexor surface at the level of skin flexion creases [1-4]. The fact that bathroom was locked from inside, negative viscera report and recovery of blade from the bathroom pointed out towards the suicidal nature of case. Cut Injury of wrist (CIW) is also known as 'Spaghetti wrists' with a minimum of three completely transected structures, a nerve, artery and a tendon [5]. Weinzweig [6] et al observed a Ulnar sided predilection of Injuries with radial artery being the most protected structure due first to web space. Ulnar triad i.e. Ulnar artery, nerve and Flexor Carpi Ulnaris was most common involved in injuries. The presentation in our case typically fits the picture, but the amount of blood found in the bathroom was baffling (Image 1-4). We will first understand the mechanism of blood spatter in CIW. The blood spatter in CIW is 'Projectile type' caused by arterial spurting of blood when a major artery is severed. The blood is propelled out of the breached vessel after being pumped out by beating of heart in an arc like pattern consisting of large individual stains [7]. This continued blood loss led to the hypovolemic shock in the deceased which happens after 15% of the total blood volume [8.9]. This is evident from the amount of the blood present in the bathroom and the soaking of clothes of the deceased in blood (Image 1-4). It implies that presence of large amount of blood was not unusual, instead such circumstances will be present in suicidal cases where the deceased cut their wrist and wait for their death by letting the loss of blood from the body. The authors intend to recommend that wherever possible the autopsy surgeon should visit the crime scene in such cases before conducting autopsy to have a fair idea about the circumstances of death and to lead the investigation towards natural course of justice.

Compliance with Ethical Standards

Funding: There was no funding involved with the study.

Conflict of Interest: There is no conflict of interests of any of the author.

Ethical Approval: This article does not contain any studies with human participants performed by any of the authors.

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