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Identification of Synthetic Perfume by Infrared and Optical Properties

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Abstract

The infrared spectroscopy is an important analytical technique in perfume industry. Polarimetry is used consistently in quality control within the pharmaceutical industry, nevertheless, the systematic evaluation of origin specific enantiomers has proved to be a valuable criterion for differentiation natural aroma from those of synthetic origin .In this study, the optical activity and the infrared spectrum of some perfume oil mixtures is obtained, the functional groups, the principal chemicals in the studied products are determined and their side effects on humans health are clarified.

Keywords: Infrared spectra, Enantiomers, Optical Activity, Optical Isomers

1 INTRODUCTION

The first evidence of the use of fragrances by mankind dates back to the ancient Egyptian civilizations around 2400 B.C [1]. Odors and aromas that we smell all around us are volatile organic compound flowers, plants and trees. 90% of fragrances are synthetic chemical, with as many as 7000 VOCs .VOCs are present in gas or vapor so enter the body by breathing .Some are absorbed by the upper respiratory system. Others, depending on the size and mass are able to reach deep into the lungs .VOCs can be carried by the blood stream to a variety of organs

(liver, kidney) or systems (central nervous system and circulatory) depending on their chemical properties (solubility in blood. Volatility to escape blood and their ability to be broken down).they may cause, eye irritation. Watering ,Nose irritation, throat irritation ,headaches ,nausea, vomiting ,dizziness ,Asthma exacerbation ,cancer ,liver damage ,kidney damage ,central nervous system. VOCs are also emitted by thousands of products in our Workplaces, like cleaning supplies, building materials, carpeting and furnishings, office equipment such as, correction fluids carbonless copy papers, photographic solutions permanent markers and Fuels. The Standard or Guidelines of TVOCs mixture for Indoor Air Quality Association is around 3.0 mg/m^3 [2].

The origin of the infrared spectrum

IR spectroscopy -is an analytical technique which helps determine molecules structure. IR spectroscopy measures the *bond vibration frequencies* in a molecule and is used to determine the functional group [3]. In the most basic terms, the infrared spectrum is formed as a consequence of the absorption of electromagnetic radiation at frequencies that correlate to the vibration of specific sets of chemical bonds from within a molecule .The amount of light absorbed by the sample is measured as wavelength is varied. The distribution of energy possessed by a molecule at any given moment, defined as the sum of the contributing energy terms (Equation 1):

$$E_{total} = E_{electronic} + E_{vibrational} + E_{rotational} + E\text{translational} \quad (1)$$

The translational energy relates to the displacement of molecules in space as a function of the normal thermal motions of matter. Rotational energy, which gives rise to its own form of spectroscopy, is observed as the tumbling motion of a molecule, which is the result of the absorption of energy within the microwave region. The vibrational energy component is a higher energy term and corresponds to the absorption of energy by a molecule as the component atoms vibrate about the mean center of their chemical bonds. The fundamental requirement for infrared activity, leading to absorption of infrared radiation, is that there must be a net change in dipole moment during the vibration for the molecule or the functional group under study. Infrared spectroscopy exploits the fact that molecules absorb specific frequencies that are characteristic of their structure (the frequency of the absorbed radiation matches the frequency of the bond or group that vibrates).

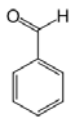
Optical activity

The orientation of atoms within a molecule is very specific. Molecules with exactly the same molecular formula, but with one atom oriented differently about a carbon atom, can have very different properties. These molecules are said

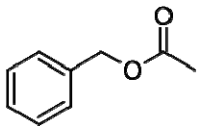
to be chiral and each form is called an enantiomer [6]. Enantiomers have identical physical properties such as boiling point, melting point, and spectroscopic features [3]

However enantiomers may possess different aroma and flavor characteristics that can affect quality of essential oils and flavor extract. Chiral compounds frequently occur in plant extracts such as essential oils and flavoring agents. These compounds exist as optical isomers, or enantiomers, which are non-super impossible mirror images of one another and differ only in their interaction with polarized light [6]. Enantiomers may also exhibit differences in toxicity and biological activity. Compounds occurring in nature typically exist as one predominant optical form samples containing an excess of one enantiomer of a chiral molecule, can rotate the orientation of plane-polarized light. Such substances are said to have optical activity. Measurement of this change in polarization orientation is called polarimetry, and the measuring instrument is called a polarimeter. Sample that contains only one enantiomer of a chiral molecule is said to be optically pure. The enantiomer that rotates light to the right, or clockwise when viewing in the direction of light propagation, is called the dextrorotatory (d) or (+) enantiomer, and the enantiomer that rotates light to the left, or counterclockwise, is called the levorotatory (l)or (-)enantiomer substances which contained an asymmetric carbon atom (i.e. a carbon atom directly united to four different atoms or radicals) were capable of rotating the plane of polarization of a beam of polarized light, has now become a fundamental theory of organic chemistry. The majority of essential oils contains one or more components containing such a carbon atom, and so possesses the power of effecting this rotation. In general, the extent to which a given oil can produce this effect is fairly constant, so that it can be used, within limits, as a criterion of the purity or otherwise of the oil. These measurements are useful for studying the structure of anisotropic materials, and for checking the purity of chiral mixtures [4].Most of enantiomers do not smell the same, while some do have identical or extremely similar odors, a sample that contains only one enantiomer of a chiral molecule is said to be optically pure. The molecules of two different enantiomers give exactly the same infrared spectra [5].

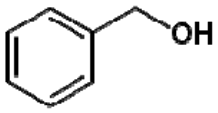
Principal chemicals found in scented products:



BENZALDEHYDE/ in: perfume, cologne, hairspray, laundry bleach, deodorants, detergent, Vaseline lotion, shaving cream, shampoo, bar soap, dishwasher detergent. Local anesthetic, are irritation to the mouth, throat, eyes, skin, lungs, and causing nausea and abdominal pain, May cause kidney damage.

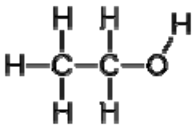


BENZYL ACETATE/ in: perfume, cologne, shampoo, fabric softener, stickup air freshener, dishwashing liquid and detergent, soap, hairspray, bleach, after shave, deodorants Carcinogenic (linked to pancreatic cancer).From vapors: irritating to eyes and respiratory passages, exciting cough. It can be absorbed through the skin causing systemic effects.

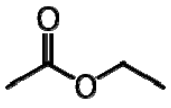


BENZYL ALCOHOL/ in: perfume, cologne, soap, shampoo, nail enamel remover, air freshener, laundry bleach and detergent, Vaseline lotion, deodorants, fabric softener are irritating to the upper respiratory tract headache, nausea, vomiting, dizziness, drop in blood pressure.

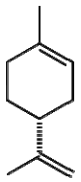
CAMPHOR / (naturally is optically active) in: perfume, shaving cream, nail enamel, fabric softener, dishwasher detergent, nail color, stickup air freshener are local irritant and readily absorbed through body tissues .Cause irritation of eyes, nose and throat dizziness, confusion, nausea, twitching muscles and convulsions.



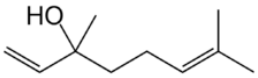
ETHANOL/ in: perfume, hairspray, shampoo, fabric softener, dishwashing liquid and detergent, laundry detergent, shaving cream, soap, Vaseline lotion, air fresheners, nail color and remover, paint and varnish remover. Ethanol vapors can have effects similar to those characteristic of ingestion.



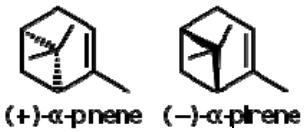
ETHYL ACETATE/ in: after shave, cologne, perfume, shampoo, nail color, nail enamel remover, fabric softener, dishwashing liquid. Are irritating to the eyes and respiratory tract may cause headache and narcosis (stupor).



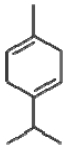
LIMONENE / (naturally is optically active) in: perfume, cologne, disinfectant spray, bar soap, shaving cream, deodorants, nail color and remover, fabric softener, dishwashing liquid, air fresheners, after shave, bleach, paint and varnish remover. It is Carcinogenic. Prevent its contact with skin or eyes because it is an irritant and sensitizer.



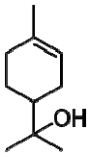
LINALOOL/ (naturally is optically active) in: perfume, cologne, bar soap, shampoo, hand lotion, nail enamel remover, hairspray, laundry detergent, dishwashing liquid, Vaseline lotion, air fresheners, bleach powder, fabric softener, shaving cream, after shave, solid deodorant. Are Narcotic respiratory disturbances and development of respiratory disturbances leading to death?



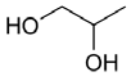
α-PINENE/ (naturally is optically active) in: bar and liquid soap, cologne, perfume, shaving cream, deodorants, dishwashing liquid, air freshener. Are Sensitizer cause damaging to the immune system.



γ-TERPINENE/ (naturally is optically active) in: cologne, perfume, soap, shaving cream, deodorant, air freshener. It is Causes asthma.

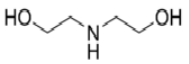


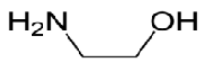
α-TERPINEOL/ (naturally is optically active)in: perfume, cologne, laundry detergent, bleach powder, laundry bleach, fabric softener, stickup air freshener, Vaseline lotion, cologne, soap, hairspray, after shave, roll-on deodorant. it highly irritating to mucous membranes. Aspiration into the lungs can produce pneumonitis or even fatal edema. Can also causes excitement.

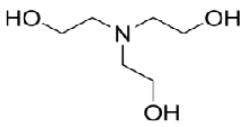


Propylene Glycol (PG) and Butylene Glycol/:)(naturally optically acive) Found in antifreeze. Acts as a "surfactant" (wetting agent and solvent).it Penetrates skin and weakens protein and cellular structure. PG penetrates the skin so quickly, the EPA warns against contact to prevent brain, liver, and kidney abnormalities.

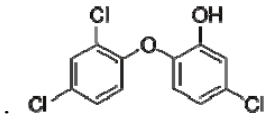
DEA (diethanolamine), MEA (monoethanolammine) and TEA (triethanolamine)



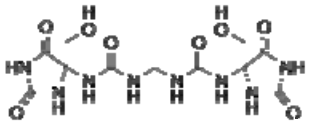




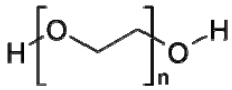
Hormone disrupting chemicals that can form cancer- causing nitrates.



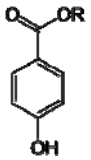
Triclosan:/ Synthetic "anti-bacterial" with a chemical structure similar to Agent Orange. It may produce dioxin, a hormone disrupting chemical with toxic effects measured in the parts per trillion; Stored in body fat, it can accumulate to toxic levels, damaging the liver, kidneys, and lungs. It can also cause paralysis, brain hemorrhages and heart problems.



DMDM & Urea (Imidazolidinyl): (naturally is optically active)Two of many preservatives that often release formaldehyde which cause joint pain, skin reactions, allergies, depression, headaches, chest pains, ear infections, chronic fatigue, dizziness, and loss of sleep. Other side effects include weakening the immune system and cancer.



Polyethylene Glycol (PEG): Carcinogenic petroleum ingredient that reduces the skin's natural moisture.



Parabens any parabens:/ It's a strong hormone disrupting chemical. Has direct links to breast cancer and heart problems.

Results and discussion

Natural perfumes are combination of different extracted oil almost from herbs with certain chemicals as solvent and others as fixatives to play very important role in reduce healthy risks. Fixative substances are work as slower down the volatile evaporation to produce better smell as well to prevent any spots residue on skin or clothes and then to reduce any risks. On other side artificial perfumes that are manufactured and sell in Iraqi market are based on mixed different chemicals are usually toxic by touching or breathing in ethanol as solvent, without any fixatives substances. These artificial perfumes undergo reasonable evaporation to give acceptable smelling but unfortunately left behind them certain residue on skins or clothes as spots, which increase the possibility to absorb by skin. Our research is based on detect the degree of unsaturated by ignition test and we receive positive result as well the TLC test shows these perfumes are mixture of different organic compounds with different polarity. Using IR spectrometer shows that the four mixtures are nearly the same components but more possible with different ratio as present in spectra 1, 2, 3, 4.

Using polarimeter with sodium lamp shows that the orientation of the polarized light is not rotated after passing through the different perfume samples. This means that the samples not contains an excess of on enantiomer of a chiral molecule, that is they are not optically active .Since pure Compounds occurring in nature typically exist as one predominant optical form and there optical activities differ from zero .the studied mixtures are of synthetic origin, with no natural flavors.

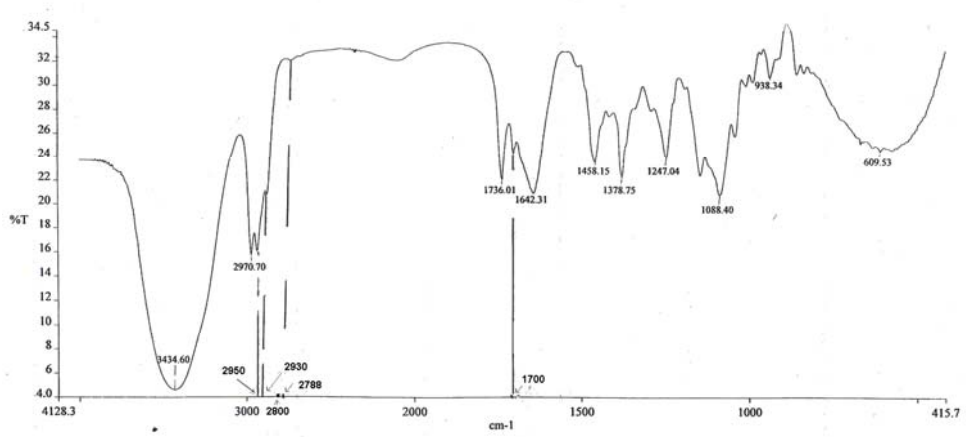


Fig. (1) Infrared spectrum of BOSS HUGO BOSS .

Table 1. Infrared vibrations of BOSS HUGO BOSS .

ν, Observed (cm^{-1})	Function group assignment
3434.60	More possible: O-H stretching of alcohol (broad band) and may be of phenol.
2970.70; **2950;2930**	C-H stretching of –CH3 and –CH2 groups.
2780	as weak shoulder C-H stretching of aldehydic hydrogen.
1736.01	C=O stretching of ester. Shoulder nearly at **1700 cm^{-1}** more possible of C=O stretching of aromatic aldeyhde or may be ketone.
1642.31	more possible C=O stretching of amide or may be C=C stretching of alkene as well may be of N-H bending of amid or amine
1458.15	C-H bending of –CH2- group.
1378.75	bending C-H of methyl group.
1247.04	more possible of C-O stretching of ester
1088.40	more possible of C-O alcohol or phenol.
938.34	C-H bending of alkene
609.53	more possible C-Cl stretching of alkyl or aryl halide and may be color

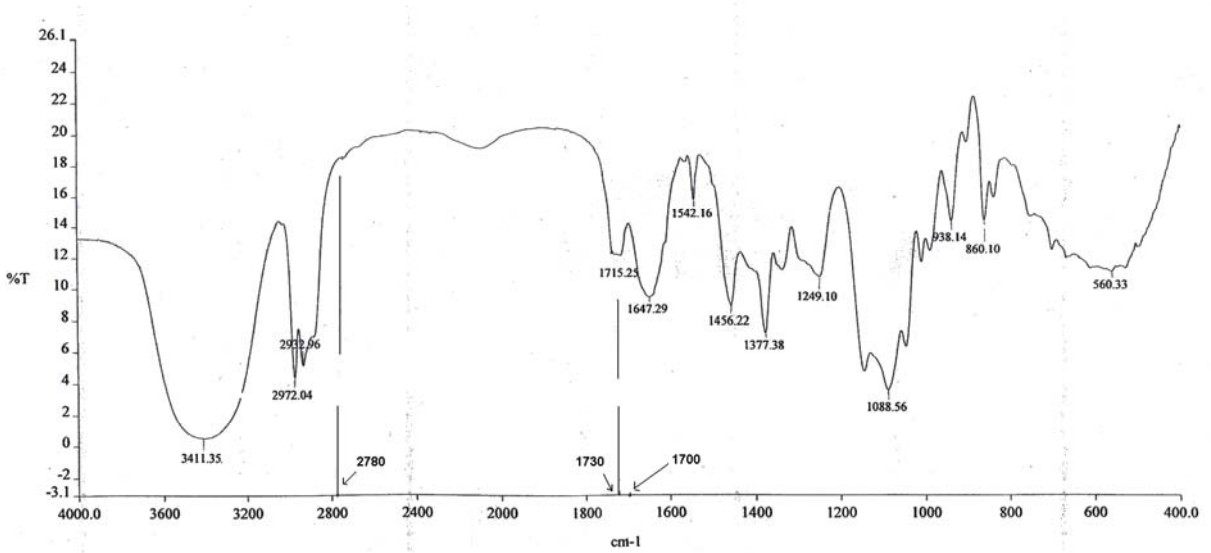


Fig.(2) Infrared spectrum of N^{O}5 CHANEL .

Table 2. Infrared vibrations of N^{O}5 CHANEL .

ν, Observed (cm^{-1})	Function group assignment
3411.35	More possible : O-H stretching of alcohol (broad band) and may be of phenol.
2972.04; **2932.96**	C-H stretching of –CH3 or –CH2 groups
2780	as weak shoulder C-H stretching of aldehydic hydrogen.
1730	as weak shoulder of C=O stretching of ester.
1715.25	more possible of C=O stretching of aromatic aldeyhde or may be ketone.
1647.29	more possible C=O stretching of amide or may be C=C stretching of alkene as well as may be of N-H bending of amide or amine.
1542.16	more possible C=C stretching of aromatic ring or may be of N-H bending of amide.
1456.22	C-H bending of –CH2- group
1377.38	bending C-H of methyl group
1249.10	more possible of C-O stretching of ester.
1088.56	more possible of C-O of alcohol or phenol.
938.14	C-H bending of alkene.
860.10	C-H bending of aromatic ring.
560.33	more possible C-Cl stretching of alkyl or aryl halide and may be color.

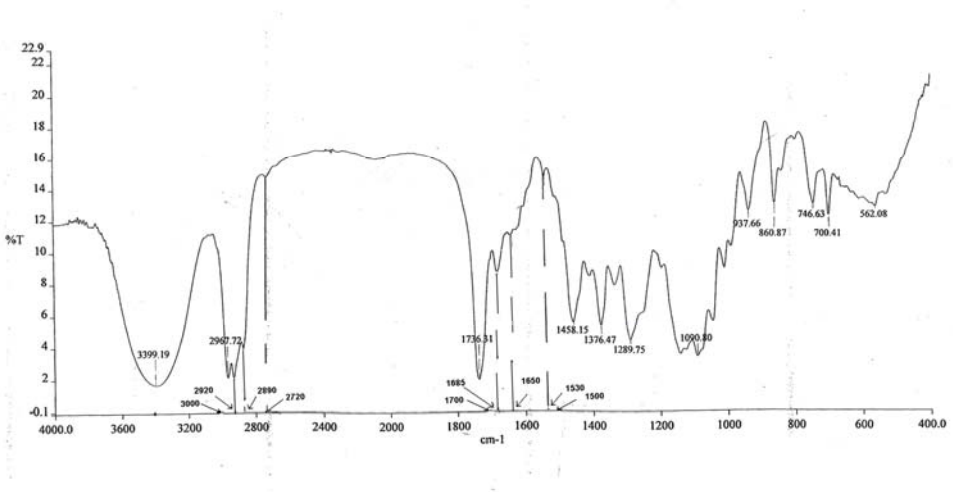


Fig (3). Infrared spectrum of MISS DIOR.

Table3. Infrared vibrations of MISS DIOR.

ν, Observed (cm^{-1})	Function group assignment
3399.19	More possible : O-H stretching of alcohol (broad band) and may be of phenol.
2967.72; **2920;2890**	C-H stretching of –CH3 and –CH2 groups.
2720	as weak shoulder C-H stretching of aldehydic hydrogen.
1736.31	more possible C=O stretching of ester.
1685	as shoulder more possible of C=O stretching of aromatic aldeyhde or may be ketone.
1650	weak shoulder,, more possible C=O stretching of amide or may be C=C stretching of alkene as well as may be of N-H bending of amide or amine.
1530	weak band more possible C=C stretching of aromatic ring or may be of N-H bending of amide.
1458.15	C-H bending of –CH2- group
1376.47	bending C-H of methyl group.
1289.75	more possible of C-O stretching of ester.
1090.80	more possible of C-O of alcohol or phenol.
937.66;700.41	C-H bending of alkene.
860.87;746.63	C-H bending of aromatic ring .
562.08	more possible C-Cl stretching of alkyl or aryl halide and may be color.

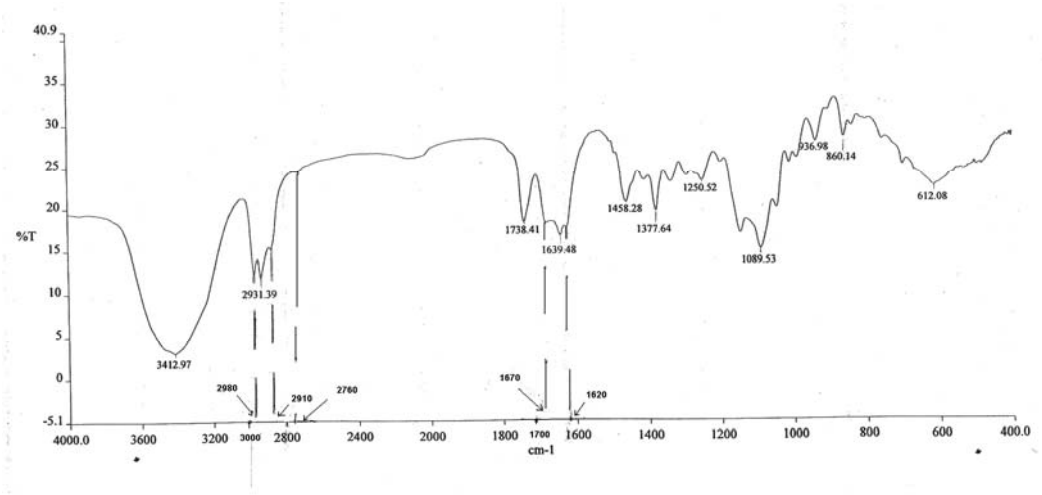


Fig.(4) Infrared spectrum GUCCI RUSH.

Table 4. Infrared vibrations of GUCCI RUSH

ν, Observed (cm^{-1})	Function group assignment
3412.97	More possible : O-H stretching of alcohol (broad band) and may be of phenol.
2980; **2931.39;2920**	C-H stretching of –CH3 and –CH2 groups.
2760	as weak shoulder C-H stretching of aldehydic hydrogen.
1738.41	more possible C=O stretching of ester.
1670	as shoulder more possible of C=O stretching of aromatic aldeyhde or may be ketone.
1639.48	more possible C=O stretching of amide or may be C=C stretching of alkene as well as may be of N-H bending of amide or amine.
1620	weak band more possible C=C stretching of aromatic ring or may be of N-H bending of amide.
1458.28	C-H bending of –CH2- group
1377.64	bending C-H of methyl group.
1250.52	more possible of C-O stretching of ester.
1089.53	more possible of C-O of alcohol or phenol.
936.98	C-H bending of alkene.
860.14	C-H bending of aromatic ring

Table 5. **Optical activity of the Perfume oil mixture samples.**

Oil Mixtures	Optical Activity (degree)
BOSS HUGO BOSS	**Zero**
N^{O}5 CHANEL .	**Zero**
MISS DIOR	**Zero**
GUCCI RUSH	**Zero**

Conclusions:

The spectra are more possible corresponding to mixtures contains different part of the following compounds:

1. Alcohols: benzyl alcohol ; ethanol ;linalool ; terpineol ;glycol ;ethanolamine ;triclosan ; imidazolidinyl ; parabens.
2. Hydrocarbons : limonene ; pinene ; terpinene.
3. Aldehydes and ketones: benzaldehyde ; camphor.
4. Esters : benzylacetate ; ethylacetate ; parabens.
5. Amides : imidazolidinyl

The results show that the orientation of the polarized light is not rotated after passing through the different perfume samples. This means that the samples not contains an excess of on enantiomer of a chiral molecule, that is they are not optically active .Since pure Compounds occurring in nature typically exist as one predominant optical form and there optical activities differ from zero .the studied mixtures are of synthetic origin, with no natural flavors.

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