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Discrimination of Saffron available in local markets Using Spectroscopic methods

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Abstract: *Saffron is known for its diverse uses and importance in the global spice trade. The objective of the present work was to use Inductive Couple Plasma Optical Emission Spectroscopy (ICP OES) and Infrared spectroscopy methods to examine the possibility to discriminate the different types of Saffron available in Kurdistan markets, to study which of these products are natural. And to indicate if a harmful element will be found in the artificial types. The result showed that the artificial saffron available in Kurdistan markets contains Lead and vanadium, which can lead to serious health problems.*
Key words: *Saffron, Inductive Couple Plasma Optical Emission Spectroscopy. Infrared spectroscopy.*

I. Introduction

Saffron is a perennial plant with botanical name of Crocus Sativus Linn is a genus in the family Iridaceae . Saffron a flower with a great coloring power which is cultivated in India, Iran, China, Spain, Greece etc. It is used for flavoring and coloring foods and it has also been used as a perfume and as a drug in ancient medicine [1]. Spice made from the dried yellowish orange 2.5-4cm long stigmas of purple-flowered saffron is considered as the world most expensive spice since harvesting saffron is very labour intensive, considering the low number of flowers per hectare and the work required for harvesting it [2]. Each blossom has three stigmas, which are picked by hand in the morning before the heat of the day, and then dried by heating or sun dried for 15-30 minutes, while the blossoms are thrown away. Approximately 1 Kg of flower is required to produce 12 g of dried Saffron spice [2, 3]

Saffron contains more than 100 volatile and aroma-yielding compounds. It also has many nonvolatile active components, many of which are carotenoids, However, saffron's golden yellow-orange colour is primarily the result of α-crocin.

Saffron has anticancer property; its interaction with DNA is studied [3]. Research on saffron's antitumor effects has been published in about 40 experimental and review articles. Just as saffron is produced in many parts of the world, so anticancer research on saffron is also a multinational effort, and involves scientists from Azerbaijan, Greece, Hungary, India, Japan, Mexico, Spain, USA and other countries. Saffron petals contain phenol and flavonoide components, apart from antioxidant positive effects on improving health, antioxidants are also added in food to prevent or delay the oxidation of food initiated by free radicals formed during their exposure to environmental factors such as air, light and temperature [5, 6]. Recently, phenolics and flavonoids have been considered as great antioxidants and proved to be more effective than Vitamin C, E and carotenoids [7,8]. The flavones seem to be the most powerful flavonoids for protecting the body against reactive oxygen species (ROS).They have also been suggested to play a protective role in liver diseases and cardiovascular diseases.

The Surprising Science Behind Saffron Extract And Weigh Loss:

The surprising science behind saffron extract and weight loss came down to the cellular level benefits of saffron acting as a neurotransmitter of the feel good hormone serotonin. Because saffron extract has the potential to increase mood and serotonin to the brain, it can dramatically lower emotional eating habits as well as better proportional control.

It is important to note that all medical weight loss science and studies regarding Saffron Extract’s ability to curb hunger and suppress appetite are supported with Satie real ingredient. Saffron Extract has many historical medicinal uses, namely to aid in; soothing irritated and upset stomachs, ease of digestion towards spicy foods, and adds the ability to potentially treat depression because of the increased serotonin levels.

The research about Satiereal Saffron Extract essentially concluded the following potential health benefits after continued used.

- Decrease in inches and weight loss
- Decrease in frequency of feeling hungry
- Decrease in fat-forming sugar cravings and snacking
- Promotes a healthy lifestyle and mood to avoid overeating [9]

II. Materials And Methodology

Four different types of saffron available in Sulaimani markets were tested:

- Sample number (1) was produced in Iran with brand bilond.
- Sample number (2): liquid saffron taste produced in India. India exports these products to Iraq in huge containers , they are later put in small containers in Alkut which is a city in eastern Iraq and putting a lable on it (made in Iraq/Alkute).
- Sample number (3) produced in Iran, Khorasan.
- Sample number (4) look like natural dry plants, it is the most cheaper type but without any lable.

Saffron Extraction:

Saffron extracted by dissolving extract of (1mg) of Saffron in 10ml of 45% by volume ethanol, after evaporation of the solvent natural Saffron oil obtained. .

Saffron extract from the natural types was prepared in School of science , chemistry department, Faculty of Science and science Education, University of Sulaimani, Kurdistan region, Iraq.

Inductive Couple Plasma Optical Emission Spectrometer (Icp Oes): available in the Kurdistan institution for strategic studies and scientific research. used for detecting metals and non-metals constitute of the samples depending on the standards available in their Laboratory.

Infrared Spectra: obtained using FT-IR LR 64912C Spectrometer/Perkin Elmer UK, in the same department.
Optical Activity: The polarimeter with sodium lamp detector used to study the optical activities of the studied food flavorings.

III. Results

A /Results Obtained By Inductive Couple Plasma(Icp):

Table (1): The ICP results

Elements	Sample (1) (ppm)	Sample (2) (ppm)	Sample(3) (ppm)	Sample(4) (ppm)
Pb	0.00	1.76	0.00	0.00
As	0.0035	0.00	0.004	0.05
Se	0.00	0.00	0.00	0.00
Ni	0.02	0.00	0.021	0.014
Cr	0.001	0.25	0.001	0.00
Sr	0.01	0.00	0.014	0.58
V	0.00	0.13	0.00	0.00
Mo	0.0065	4.45	0.007	0,00
Zn	0.08	0.42	0.086	0.93
Mg	1.214	4.31	1.216	1.364
Fe	0.07	0.55	0.073	0.096
Ca	3.385	0.00	3.492	7.683
Na	5.40	30.59	5.410	9.053
K	19.015	14.14	19.01	41.70

A-Results Obtained By Using Infrared Spectra:

- For sample number 1

Figure (1): sample 1

Table(2) Vibration assignment of natural Saffron; sample(1)

3410.81 ν, Observed cm^{-1}	Function group assignment
2925.27	C-H stretching of –CH3 and –CH2 groups.
2840	As weak shoulder C-H stretching of aldehydic hydrogen.
1690	As weak shoulder more possible of C=O stretching of conjugated aldeyhde .
1654.04	C=C stretching of alkenes.
1450	C-H bending of CH2 or may be of CH3..
1410	O-H bending of alcohol.
1375.90	C-H bending of aldehydic hydrogen or may be of O-H bending alcohol.
1227.90 ;1072.61	More possible of C-O alcohol or ether.

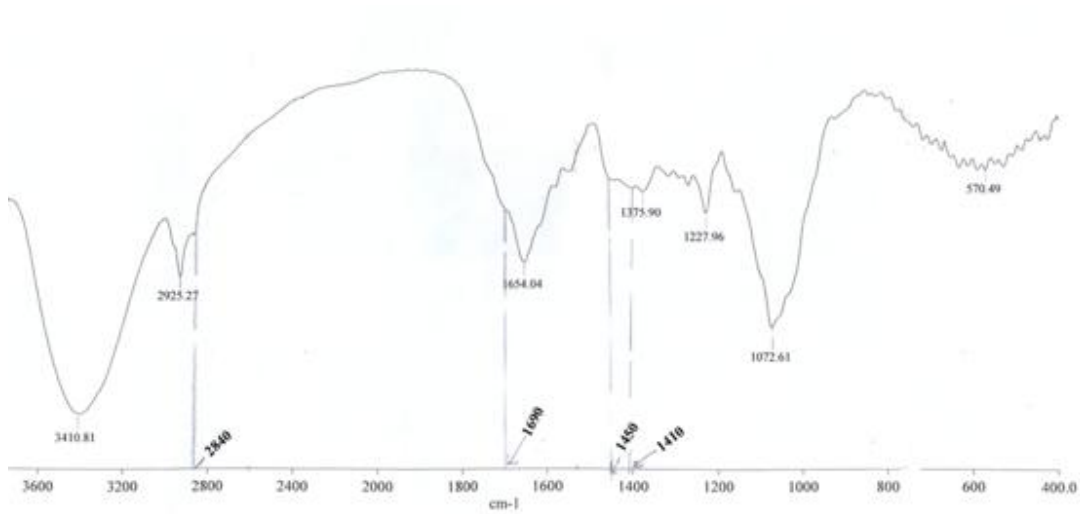


Figure (2): Infrared spectrum of Saffron sample(1)

- For sample number 2

Figure (3): sample 2

Table(3): Vibration assignment of artificial Saffron; sample(2) Saffron tests

ν, Observed (cm^{-1})	Function group assignment
3467.43	More possible: O-H stretching of alcohol (broad band) and may be of phenol.
3050	C-H stretching of aromatic ring
2980 ; 2850	C-H stretching of alkane.
1643.00	C=C stretching of aromatic ring in mesomeric form.
1530	As weak shoulder of N=N stretching of conjugated azo compound.
1500	More possible C=C stretching of aromatic ring.
1055	S-O stretching of sulfonate.

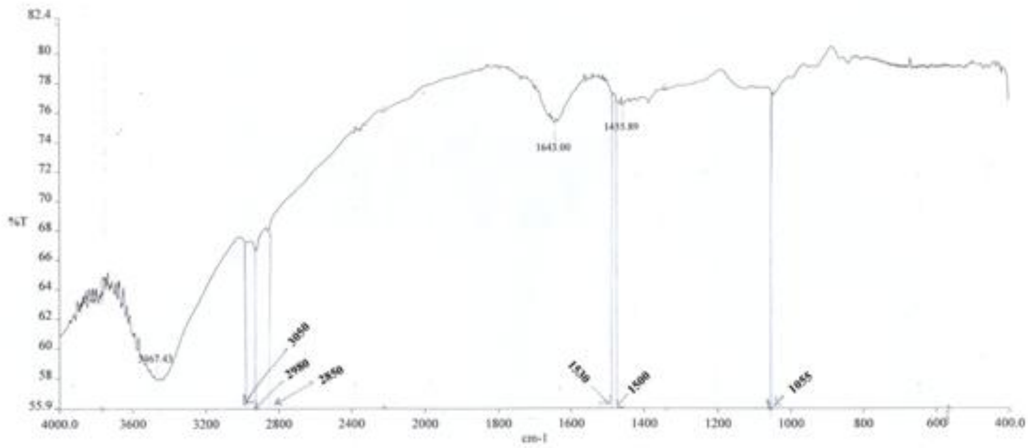


Figure (4): Infrared spectrum of Saffron sample(2)

- For sample number 3

Figure (5): sample 3

Table(4): Vibration assignment ofnatural Saffron; sample(3)

ν, Observed (cm^{-1})	Function group assignment
3412.76	More possible: O-H stretching of alcohol (broad band) and may be of phenol.
2922.73	C-H stretching of –CH3 and –CH2 groups.
2830	As weak shoulder C-H stretching of aldehydic hydrogen.
1690	As weak shoulder more possible of C=O stretching of conjugated aldeyhde .
1654.07	C=C stretching of alkenes.
1381.93	O-H bending of alcohol.
1228.93 ;1072.58	More possible of C-O alcohol or ether.

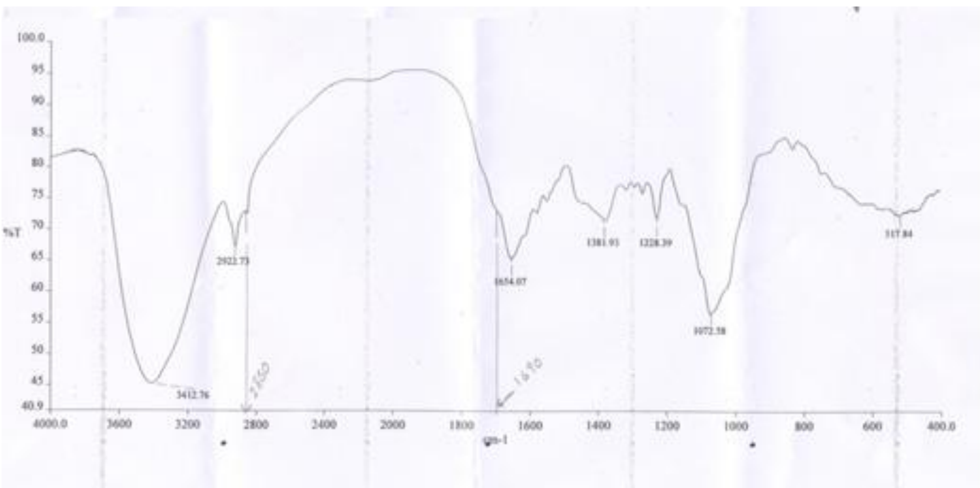


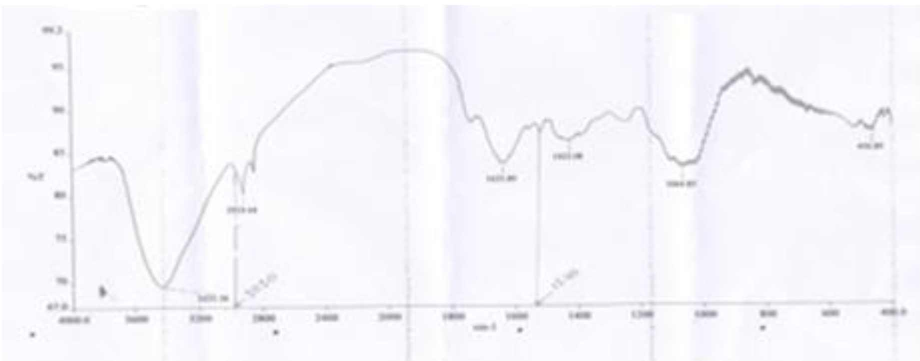
Figure (6): Infrared spectrum of Saffron sample(3)

- For sample number 4

Figure (7): sample 4

Table(5): Vibration assignment of Saffron; sample(4)

ν, Observed (cm^{-1})	Function group assignment
3435.58	More possible: O-H stretching of alcohol (broad band) and may be of phenol.
3030	As weak shoulder C-H stretching of aromatic ring
2918.64	C-H stretching of alkane.
1635.69	C=C stretching of aromatic ring in mesomeric form.
1423.O8	O-H bending of alcohol.
1064.85	S-O stretching of sulfonate .



Figure(8): Infrared spectrum of sample (4)

IV. Conclusion

1. Due to the results obtained using inductive couple plasma optical emission spectrometer (ICP)The concentration of metals and non metal elements in the tested samples are present in table (3), Lead and vanadium are the only elements that were detected in the liquid saffron taste and absent in the other samples.
2. The results show that samples (1) and (3) contain 0.001 ppm Chromium since chromium is one of the substances whose use is restricted by the European Restriction of Hazardous Substances Directive, The LD50* for chromium (VI) ranges between 50 and 150 mg/kg. And the LD50 of saffron is 200mg per Kg weight (Elsevier), one can conclude that chromium is the reason of saffron's hazardous [10].
3. The N=N stretching of Trans azo compound is difficult to appear in IR spectrum but according to Hooke's Law ($\upsilon_{bar} = 4.12 \times (K/\square)^{1/2}$) absorbs in the 1557.21 cm^{-1}

$$\upsilon_{bar}(N = N) = 4.12 \times \left([10 \times 10^5 / 14 \times 14/(14 + 14)]\right)^{1/2} = 1557.21 cm^{-1}$$

4. From the IR spectrum Sample (4) we concluded that it was a fake type of saffron, it was some unknown dried natural plant with an excess of Red 40 as dyes to give it saffron's color.
5. As a result of the IR Vibrations assignments the molecular structure of samples 1 and 3 which were 100% natural are as follows.

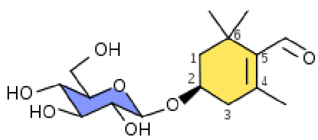


Figure (9): Molecular structure

6. Samples number 2 and 4 with N=N stretching of conjugated azo compound at 1530 and 1540 cm^{-1} respectively posses the following structures

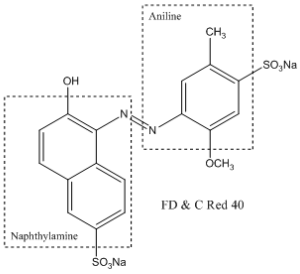


Figure (10): Sample structure with N=N stretching of conjugated azo compound at 1530 and 1540 cm^{-1}

7. Using polarimeter with sodium lamp detector we concluded that samples (1) and (3) were %100 natural.

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* LD50 / Letal dose first known use on1945,it is the amount of toxic agent (as poison ,virus ,or radiation)that is sufficient to kill 50 percent of a population of animals usually within a certain time.