Detecting Adulteration of Durum Wheat Pasta by FT-IR Spectroscopy

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Abstract: Hard wheat flour and durum of different extraction level (whole meal, 82% and 72%) and their pasta products were evaluated by the ordinary methods in parallel with FT-IR spectroscopy. Chemically, there was considerable difference between hard wheat flour and durum in protein and crude fiber contents. Durum whole meal, hard wheat flour (72%) and durum adulterated with hard wheat flour 72% (1:1) were used to prepare high quality pasta and adulterated pasta, respectively. Color analysis showed that, addition of hard wheat to durum increased the lightness values but decreased the redness and yellowness values. Also, pasta processed from these raw materials had the same character except lightness. Cooked pasta had no significant differences in lightness and redness values while there were significant differences in yellowness values of the cooked pasta. Sensory evaluation of pasta made from durum and hard wheat and their mixture showed that, there were significant differences between them in all sensory properties. Cooking quality of pasta revealed that, the weight of hard wheat pasta increased more than durum pasta, while, the volume of durum pasta was higher than hard wheat pasta. Cooking loss was very lower in durum pasta than hard wheat pasta. Since, wheat and their products contain different polar functional groups such as lipids, carbohydrates and proteins, FT-IR spectroscopy was used as a beneficial tool for detecting adulteration of pasta. The FT-IR results showed that hard wheat (72%) was recognized from durum (72%) by presence of two specific bands at 1420 and 1375 cm^{-1} which are nearly disappeared in durum, while durum was characterized by two absorption bands at 2857 and 1745 cm^{-1}. FT-IR spectral analysis of durum pasta and adulterated ones showed the same results of durum and wheat flour raw materials.

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1. Introduction

Pasta is one of popular wheat products worldwide, manufactured from special type of wheat known as durum wheat that gives the required quality of the pasta (Sisson, 2008). Most countries legislation stipulates that pasta must be made from *(Triticum durum*) semolina. Addition of common wheat is the most common adulteration in industrially made pasta. Food authenticity is a subject of serious concern to the consumers and food authorities, where correct and adequate labeling of food composition has become crucial. Besides the composition of specific foods is always a key factor in the quality of the final product (Aktas *et al*., 2009; Gupta and Panchal, 2009; Terzi *et al*, 2003*)*. Different techniques have been used to determine the level of common wheat adulteration in pasta, but methods concerning sitosterol palmitate (Matveff, 1952) or water soluble proteins specific to common wheat (Resmini, 1968; Garcia *et al*, 1969; Feillet and Kobrehel, 1972) were not specific enough or not sensitive enough. Recently, several methods had been invented to investigate adulteration of durum wheat pasta, these included near infrared spectroscopy (Cocchi *et* al, 2006); immunoassay (Stevenson *et al*, 1994) and polymerase chain reaction (PCR) method (Alary *et al* 2002). Near Infrared spectroscopy is a widespread technique used in many fields of analytical chemistry including the quality control of foodstuffs (Bertrand *et al*, 1985; Sirieix and Downey 1993; Shenk *et al*, 2001 and Barton *et al*, 2000). In the field of cereal analysis, NIR spectroscopy being successful in modeling many quality variables such as protein, moisture, dietary fiber contents and wheat hardness (Manley *et al*, 2002; Osborne, 2000).

In present work, FT-IR spectroscopic technique was applied to differentiate between two Egyptian wheat varieties and to detect the adulteration of durum pasta in parallel with the common evaluation methods of chemical composition, color parameters, cooking quality and sensory evaluation.

2. Materials and Methods

Hard wheat (Sakha 93) and durum wheat (Sohage 3.) were obtained from Field Crops Department, Agricultural Research Centre, Ministry of Agriculture, Giza, Egypt. The properties of the selected samples were identified using chemo-physical methods in parallel with FT-IR Spectroscopy.

The moisture, proteins, carbohydrates, fats, fiber and ash content in wheat flour and durum were determined by A.O.A.C (1990). Color measurement (L^*, a^*, b^*) were measured using Hunter Lab. This color assessment system is based on the Hunter L^*, a^{*-} and b^* coordinates. L^* was representing lightness and darkness, + a^* redness, -a^* greenness, + b^* yellowness and - b^* blueness (Hunter, LabScan XE - Reston VA, USA). The instrument was standardization against a White Tile of Hunter Lab Color Standard (LX No.16379): X= 77.26, Y= 81.94 and Z= 88.1 before each measurement.

Cooking quality of pasta were carried out by measuring the increases in weight, volume and cooking loss after cooking according the methods of AACC (2000). Sensory evaluation of cooked un-adulterated and adulterated pasta was evaluated as described by Hallabo *et al.* (1985).

All spectra of the selected samples were measured using FT-IR spectrophotometer 6100 Jasco, Japan. All spectra were recorded in the absorbance mode (three replicates) from 400 to 4000 cm^{-1} using the KBr technique

All results were evaluated statistically using analysis of variance and regression analysis as reported by McClave and Benson (1991).

3. Results and Discussion

Hard wheat and durum flour of different extraction levels (whole meal, 82% and 72%) were evaluated chemically as shown in Table (1). The obtained results indicated that, there was slight difference between hard wheat flour and durum in total carbohydrate, fat and ash contents. A considerable difference between them was observed in their protein and crude fiber contents. In other word, gross chemical composition represented the nutrient contents of wheat varieties but was not suitable to differentiate between them.

Table (1): Gross chemical composition of durum and hard wheat (dry weight basis %).

Varieties	Moisture	Total Car.	protein	Crude fiber	fat	Ash
Durum wheat (Sohage 3)						
Whole meal	11.92± 0.18	80.97± 0.29	13.3± 0.29	1.69± 0.05	2.52± 0.09	1.51± 0.03
82%	11.65± 0.25	83.53± 0.05	12.05± 0.13	1.12± 0.03	1.81± 0.08	1.47± 0.03
72%	10.13± 0.17	86.33± 0.29	10.57± 0.28	0.66± 0.01	1.62± 0.04	0.8± 0.04
Hard wheat (Sakha 93)						
Whole meal	13.61± 0.51	80.38± 0.57	11.81± 0.33	3.46± 0.22	2.52± 0.09	1.81± 0.06
82%	13.14± 0.13	84.16± 0.25	11.04± 0.04	1.47± 0.07	0.81± 0.08	1.51± 0.06
72%	12.83± 0.36	86.39± 0.16	10.42± 0.13	0.91± 0.11	1.62± 0.04	0.64± 0.06

Data represent mean of three replicate sample ± standard deviation.
Total Car. = Total carbohydrate.

Pasta made from durum wheat of superior quality results in a bright yellow color and it retains, after cooking, firmness and absence of stickiness. Bright yellow color of pasta is an important prerequisite for customers. Table (2) shows the color attributes of raw material (durum or durum replaced with hard wheat), uncooked and cooked pasta. Data in the table indicated that addition of hard wheat to durum increased the lightness values but decreased the redness and yellowness values. This may be due to the higher content of carotenoids in durum than hard wheat. Also, pasta processed from these raw materials had the same observation except lightness, as the lightness of pasta made from wheat flour decreased than pasta made from durum. Cooked pasta had no significant differences in lightness and redness values while there were significant differences in yellowness values of the cooked pasta. These results could be attributed to the different solubility behavior of pigments. This leads to the leaching of white and red pigments in cooking water.

Table (3) shows the sensory evaluation of pasta made from durum and hard wheat and their mixture. There were significant differences between the tested samples in all tested properties i.e. appearance, color, flavor, tenderness and stickiness. Pasta made from durum had the highest score for appearance and color. This is due to the higher content of carotenoids compared with pasta made from hard wheat. Also, pasta made from durum had the highest score for tenderness and the lowest score for stickiness. This could be attributed to the strong gluten network in durum wheat compared with hard wheat.

Table (2): Effect of replacing durum with hard wheat on color quality of pasta.

Samples	L*	a*	b*
Raw materials			
100% Durum	87.88^{c}±0.129	1.42^{a}±0.072	17.79^{a}±0.37
75% durum	84.72^{d}±0.133	1.15^{b}±0.025	14.17^{b}±0.28
50% durum	90.92^{b}±0.096	0.93^{c}±0.057	12.57^{c}±0.13
100% hard wheat	92.11^{a}±0.129	0.59^{d}±0.113	11.17^{d}±0.128
LSD	0.212	0.073	0.467
Uncooked pasta			
100% Durum	76.89^{a}±0.38	2.8^{a}±0.035	18.83^{a}±0.067
75% durum	76.72^{a}±0.133	2.45^{b}±0.065	17.39^{b}±0.31
50% durum	76.59^{a}±0.35	2.21^{c}±0.09	17.22^{b}±0.068
100% hard wheat	75.52^{b}±0.89	1.94^{d}±0.21	16.25^{c}±0.86
LSD	1.05	0.223	0.862
Cooked pasta			
100% Durum	61.31^{a} ±0.53	1.16^{a}±0.041	18.66^{a}±0.18
75% durum	60.16^{a}±0.31	1.11^{a}±0.021	18.93^{a}±0.15
50% durum	57.85^{a}±0.25	1.17^{a}±0.032	17.24^{b}±0.21
100% hard wheat	59.72^{a}±0.31	1.16^{a}±0.04	15.72^{c}±0.31
LSD	3.66	0.197	0.977

Table (3): Effect of replacing durum with hard wheat on sensory quality of pasta

Sample	Appearance (10)	Color (10)	Flavor (10)	Tenderness (10)	Stickiness (10)
100% Durum	8.4^{a}	8.2^{a}	8.8^{a}	8.3^{a}	6.5^{c}
75% Durum	7.8^{a}	7.9^{a}	8.2^{ab}	8.0^{ab}	7.3^{b}
50% Durum	7.9^{a}	7.4^{a}	7.8^{bc}	7.2^{bc}	7.7^{ab}
100% Hard wheat	7.0^{b}	6.3^{b}	7.4^{c}	6.4^{c}	8.3^{a}
LSD at 0.05	0.78	0.87	0.79	0.88	0.76

Cooking quality of pasta i.e. weight increase, volume increase and cooking loss are shown in Table (4). Data revealed that, the weight of pasta made from hard wheat increased more than pasta made from durum while, the volume of pasta made from durum was higher compared with those containing hard wheat. Cooking loss, the most important parameter, was very lower in pasta made from durum than that containing hard wheat. These results could be related to the strong gluten network and the milling procedure that was used for durum production compared with production of hard wheat which allowed more starch to be leached out during cooking.

Table (4): Effect of replacing durum with hard wheat on cooking quality of pasta.

Sample	Weight increase	Volume increase	Cooking loss
100% Durum	122	300	2.5
75% Durum	160	255	7.5
50% Durum	191	235	7.5
100%Hard wheat	235	215	10

Differentiation between durum and hard wheat varieties can be adopted on molecular basis by using FT-IR spectroscopy. Since wheat and its products contain different polar functional groups as lipids, carbohydrates and protein, so FT-IR spectroscopy was used as a helpful tool to identify the molecular composition. Assignments of the FT-IR absorption of wheat flour varieties (Figure 1) are tabulated in Tables (5 - 6). The obtained results showed different bands arising from NH stretching of protein, CH stretching asymmetric, amide I (C=O stretching) and amide II (C-N stretching and NH bending) at 3427 - 3393 cm^{-1}, 2929 – 2926 cm^{-1}, 1651 - 1654 cm^{-1} and 1540-1544cm^{-1}, respectively**.** Furthermore, whole meal and flours (72% and 82%) of durum, and hard wheat characterized with some bands, i.e. CH bending, C-O-C stretching, C-C stretching, C-O stretching , (C6-C5-O5-C1-O1) bond of starch and ring breezing associated with absorbance at 1458 - 1454 cm^{-1},1157 cm^{-1}, 1080 cm^{-1}, 1019-1022 cm^{-1}, 860-857 cm^{-1} and 760-764 cm^{-1}. Differentiation between wheat varieties were detected via the presence of certain peaks at about 1420 cm^{-1} (COO^{-} symmetric stretching vibration) and 1373 cm^{-1} (stretching C-OH) in hard wheat and its extracts only. Assignments of FT-IR were agreed with Williams et al., 1993, Brown et al., 1993 and HRUŠKOV and ŠVEC (2009).

FT-IR spectroscopy technique was also used to evaluate the quality of pasta, where high grade pasta was manufactured from high grade wheat type (durum). High grade durum has a high price, where it is grown in cold climate and imported from abroad so, durum could be adulterated with cheaper wheat flour. In our study, pasta was produced from 100% durum flour and adulterated durum that was replaced with 50% or 100% hard wheat flour. Careful analysis of the obtained spectra (Figure 2 and Table 7) revealed that durum pasta was characterized by presence of specific bands at 2857 cm^{-1} and 1745 cm^{-1}, which are due to CH and C=O stretching vibration, respectively. On the other hand, these absorption peaks were absent in the hard wheat pasta and appeared with very weak intensity in the adulterated pasta.

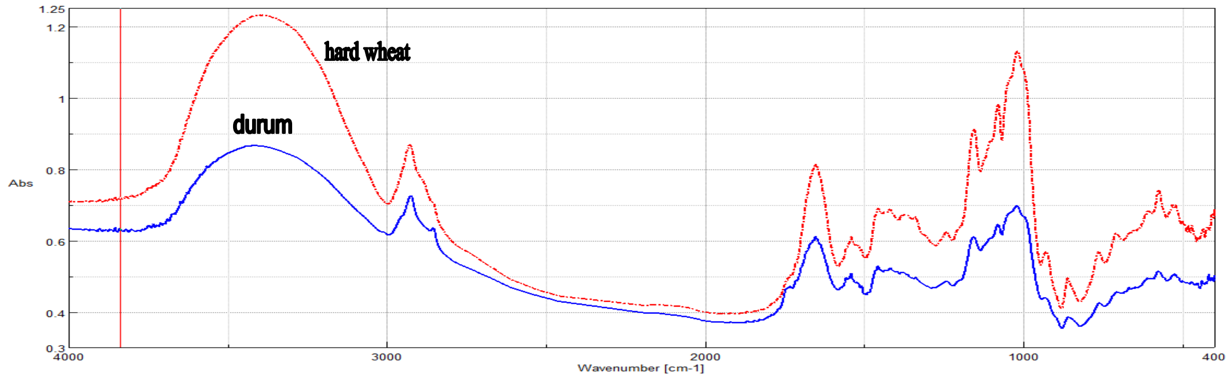

Figure (1): FT-IR spectra of durum and wheat flour 72%.

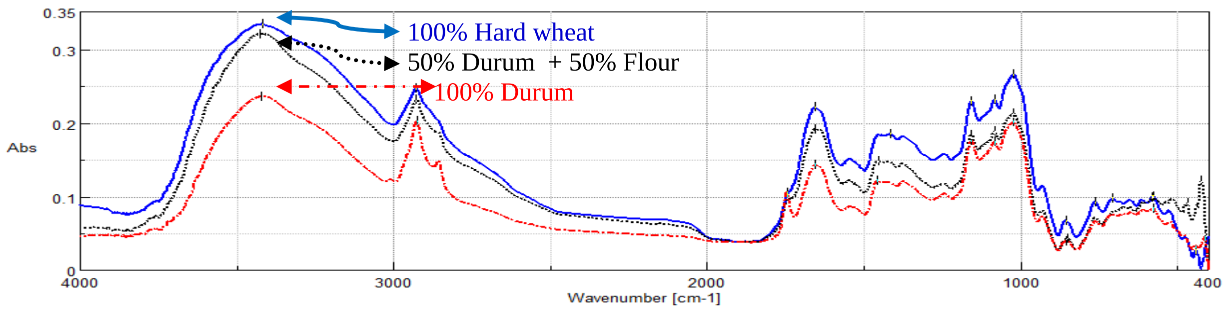

Figure (2): FT-IR peaks of adulterated pasta with hard wheat

Table (5): Assignments of FT-IR absorption bands of durum wheat and its extracts

Assignments	Whole meal	Wheat flour	
		82%	72%
NH stretching of protein	3427	3425	3419
CH stretching asymmetric	2926	2926	2926
Amide I (C=O stretching of ester)	1651	1652	1654
Amide II (C-N stretching with NH bending)	1543	1543	1543
CH bending	1457	1458	1456
C-O-C stretching of starch	1157	1158	1157
C-C stretching	1080	1081	1080
C-C stretching of starch	1021	1021	1022
Stretching C-O ring	930	930	---
(C6-C5-O5-C1-O1) ring	860	859	857
Ring breezing	763	763	760

Table (6): Assignments of FT-IR absorption bands of hard wheat and its extracts.

Assignments	Whole meal	Wheat flour	
		82%	72%
NH stretching of protein	3399	3407	3393
CH stretching asymmetric	2929	2926	2928
Amide I (C=O stretching of ester)	1651	1652	1652
Amide II (C-N stretching with NH bending)	1542	1540	1541
CH bending	1455	1455	1455
Stretching (COO-)	1420	1421	1420
Stretching C-OH	1373	1377	1374
C-O-C stretching of starch	1157	1157	1157
C-C stretching	1080	1080	1080
C-C stretching	1019	1020	1019
Stretching C-O ring	930	930	930
(C6-C5-O5-C1-O1) ring	860	860	860
Ring breezing	764	763	764

Table (7): Assignments of FT-IR absorption bands of adulterated pasta.

Identification	**Hard wheat 100%**	**Durum/Hard wheat (1:1)**	**Durum 100%**
NH stretching vibration band	3420.14	3427	3422.06
C-H, CH2 groups f lipids	2927.41	2927.41	2926.45
C-H stretching vibration	- - - - - - - -	2856.20	2857.02
C=0 ester of lipids	- - - - - - - -	1741	1745
Amide I	1656.55	1656.55	1654.62
Amide II	1547.59	1547.59	1547.59
CH2, CH3 bending vibration bands	1454.06	1454.06	1456.96
Stretching (COO-)	1420	1421	- - - - - - - -
CH2 group of amino acids	1375	1377.89	- - - - - - - -
Amide III	1243.86	1245.79	1242.9
C-O-C RING OF STARCH	1157.08	1157.08	1157.08
- - - - - - - -	1082.83	1082.83	1083.8
C-C, C-C-C bands of starch	1022.09	1023.05	1023.05
C-O, C-C, C-C-O bands of starch	931.45	931.45	930.485
TrytoPhan stretching bands	8556.239	855.454	855.275
Tryptophan stretching bands	763.673	762.709	761.744
C-S vibration band	705.819	705.819	712.569
C-H bending band	655.679	651.822	651.822
Phenyl ring	614.217	610.12	608.431
S-S Stretching band	576.612	580.469	578.54

Conclusion

Chemical and color analysis separately were not sufficient to identify and differentiate between wheat varieties (hard and durum wheat) and adulterated pasta, but sensory evaluation and cooking quality were able to detect the quality variation between them. FT-IR spectroscopy was used successfully for identifying and differentiating between two Egyptian wheat varieties (durum and hard) and was able to detect the adulteration of pasta on molecular basis.

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