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Chemical Analysis and Detection of Adulteration in Different Brands of Milk in Libyan Market

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Abstract

Adulteration and quality control of food products are international main concern. The study involves analysis of seven different brands of milk available in the Libyan markets, coded as: M1; M2; M3; M4; M5; M6; goat milk and M7; camel milk.
Three qualitative analysis were conducted; detection of starch, NaCl and $(NH_4)_2SO_4$. The results were negative except in NaCl test in M1, M2, M4 and M7. Four quantitative analysis were conducted, as most of the results were in the normal ranges but there are some exceptions. In water content, M1 88.34±0.16% and M2 88.22±0.51% were just more than the normal range of cow milk 87.3–88.1% according to United States Department of Agriculture (USDA) database. While, M7 90±0.33% was over the normal range 88.7–89.4%. In protein contents; M3 2.60±0.09% was less than the product label 3.2% and the normal range according to USDA database. In addition, M7 1.38±0.17% was less than the level 2.4–4.2%. In titratable acidity; M4 0.210±0.009% and M7 0.250±0.004% were significantly higher than the normal range according to Food and Agriculture Organization (FAO) recommendations 0.10–0.20%, which may indicate that there is a bacterial growth. In pH analysis; M4 6.28±0.03 and M7 6.11±0.01 were less than the normal range 6.3-8.5 according to Food and Drug Administration (FDA) and Center for Food Safety and Applied Nutrition (CFSAN) recommendations, which support the result of the titratable acidity. In general, M7 was the worst brand. Therefore, authorized entities should monitor all dairy products to ensure the safety and quality for the consumers.

Keywords: Adulteration, chemical analysis, Libyan market, milk.

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Introduction

Milk is considered as a complete food because it contains large quantities of required nutrients to maintain life (Fox and McSweeney, 1998). Milk consumption among mammals is common, particularly in humans, as most of them consume the milk of other mammals, mostly from cow (84%), buffalo (13%), goat (2%), and sheep (1%) (Gerosa and Skoet, 2012). Global production of milk in 2011 reached about 742.2 million tons and the world average for milk production is about 2,200 Letter /cow, as the largest producer is the USA (more than 90 million tons/year) and the greatest number of dairy cows in India (more than 40 million cows) (Bedford et al., 2012). Milk appears to be a simple white fluid, but in fact, it is a complex substance containing varieties of compounds. Composition of milk differs depending on several factors including: the species of mammal, breed, feeds of the animal, season, milking interval, health and the stage of lactation. Milk is an water in oil emulsion of oil (o/w) (dispersed phase) in water (continuous phase) contains dissolved carbohydrates, protein and minerals (FAO, 1986). In addition, milk contain a suspension of casein micelles (casein, calcium, phosphors). Milk consists of two major constituents which are water (moisture) and milk solid. Milk solids are composed of fats and milk solids-not-fat (MSNF). MSNF is composed of protein, lactose, and minerals. Milk proteins consist of caseins and whey proteins (FAO, 1986). There are a range of milk processing to preserve milk for a long shelf-life, could be days, weeks or months. To extend shelf-life of milk for several days, used methods such as cooling at low temperature or fermentation with lactic acid bacteria (Chandan, 1997). Pasteurization is a heat treatment process to kill or destroy bacterial pathogens in milk, through applying high temperatures in constant period (usually 63 °C for 30 min. or 72 °C for 15 sec.) and then packaged under sterile conditions. While pasteurized milk has a shorter shelf-life than sterilized milk. Ultra-Pasteurized milk process is similar to pasteurization but applying more temperature degree (138 °C for a minimum 2 sec.) (Chandan, 1997). Libya is one of the most principal African countries importing milk and dairy products (Muehlhoff and MacMahon, 2013). In addition, the consumption of dairy products is expected to grow significantly and there are signs that there will be significant investment in new factories in the next years (Hemme and Otte, 2010). Fresh milk does not cover the Libyan domestic market due to the low number of cattle farms. However, about 75% of total milk production is from the “non market” economy, or produced from home consumption and locally trading. Instead, the milk available in the market includes UHT, sterilized and pasteurized milk. They could be whole fat milk, reduced fat milk, or skimmed milk (non-fat milk) (Netherlands Enterprise Agency, 2018). There are some Libyan factories produced milk as recombined milk from cow powdered milk which are imported from abroad. Al Rayhan Co. and Judi Co. are dominated in the milk market by up to 50%, whilst Al Naseem Co. command in the Labneh and yogurt sectors. There are also international dairy products in the Libyan market include Egyptian, Saudi and some European companies such as Nestle, Danone and Arla (Netherlands Enterprise Agency, 2018). The chemical analysis of milk sample must be carried out immediately on receipt at the laboratory (Sudhanthiramani et al., 2015). Qualitative analysis is based on simple color during chemical reactions when adding reagents. Adulteration in foods describes as a corruption process by adding a foreign or low-grade substance to product for commercial profit (Sudhanthiramani et al., 2015). Starch is added to milk to increase its density (when water is added to milk). High amount of starch in milk may cause diarrhea due to its accumulation in the body (Sudhanthiramani, et al., 2015). Common salt (NaCl) is added to milk to mask the high

quantity of water (Sudhanthiramani, et al., 2015). It has been found that high amount of NaCl in milk could affect the pH levels or acid-base balance in the body and may lead to a reduction in acquired immunity, kidney problems and sensory disorders (Barham, et al., 2014). Ammonium Sulphate $(NH_4)_2SO_4$ is added to milk to increase its thickness (when water is added to milk). In the body, $(NH_4)_2SO_4$ is completely dissociated into the ammonium and the sulphate ions. The ammonium ion plays a key role in the maintenance of the acid-base balance. However, at high sulphate concentration in the body more than intestinal absorption lead to diarrhea (Barham et al., 2014). The common chemical analysis conduct for milk sample, include: dry matter (DM), ash content, pH, acidity percentage and protein content (Barham et al., 2014). The DM content of milk consists of all its components excluding water. Determine of water is one of the most fundamental analysis for important reasons, including: legal and labeling requirements, economic reasons (water is an inexpensive ingredient) and microbial stability (Sudhanthiramani et al., 2015). pH is a logarithmic scale to measure the strength of an acid in a solution. According to U.S. Food and Drug Administration Center for Food Safety and Applied Nutrition (FDA/CFSAN), pH value of milk ranges between 6.3 and 8.5 (US.FDA/CFSAN, 1998). TA is a measure of the amount of an acid present in a solution. Milk has traces of lactic acid (citric acid, phosphates, CO_2 and casein) with natural acidity from 0.10% to 0.20%. The increase in acidity more than 0.20% is due to the production of excess of lactic acid as a result of the bacterial growth (Draaiyer et al., 2009). In other hand, the decrease in acidity less than 0.10% may be is due to mastitis in animals (FAO, 1986). TA test more precise than alcohol test and clot on boiling test to determine the milk acidity (Draaiyer et al., 2009).

Materials and methods

The work was carried out in two parts: qualitative and quantitative analysis of 7 different brands of full fat and fresh milk available in the Libyan commercial market (Ajdabiya city), some of them are local and some imported. Five different tetra pack milk and two raw milk samples (goat and camel) were randomly selected and were analyzed in the Laboratory of Department of Chemistry at Ajdabiya University. Each brand has been analyzed at least three times to verify precision and reliability. Collection and preparation of milk samples were carried out according to AOAC procedures (Horwitz, 2000) table (1).

Table (1) :The milk samples used in the study

No.	Trade name	Sample code	Description
1	Juhayna	M1	Ultra-pasteurized milk
2	Sterilgarda	M2	UHT whole milk
3	Judi	M3	UHT whole milk
4	Berti	M4	Ultra-pasteurized milk
5	Xoia	M5	Ultra-pasteurized milk
6	Goat	M6	Fresh milk
7	Camel	M7	Fresh milk

Qualitative analysis to detect adulteration

The analysis in the study were: detection of starch, sodium chloride and ammonium sulphate. The test of iodine solution was applied to detect the presence of starch according to the method of Bureau of Indian Standards (Bureau of Indian Standards, 2003). To detect the presence of extraneous salt (NaCl), the test of silver nitrate (0.1N) and potassium chromate solution (10% w/v) was applied (Kirk et al., 1991). The test of NaOH (2%), NaClO (2%) and phenol (5%) solution was applied to detect the presence of ammonium sulphate (Azad and Ahmed, 2016; Kumar et al., 2010).

Quantitative analysis

Determination of water in milk samples

It was determined using forced air draft oven method at 100±1 ºC according to the method of AOAC. The loss in weight is the moisture content in the sample and rest was dry matter (Horwitz, 2000).

$$\% \text{ Dry matter} = \frac{(D1 - D2) \times 100}{D1}$$

D1: Weight of the sample before the drying.
D2: Weight of the sample after the drying.

$$\text{Water content \%} = 100 - \% \text{ Dry matter}$$

Determination of total protein in milk samples

It estimated by formal titration method (Pyne's method). The method based on the titration of the sample (adding potassium oxalate and phenol phthalein indicator) with 0.1 N NaOH solution. The second titration is applied by adding formalin into the sample, then again titrate with NaOH. Then 3rd titration (blank) is conducted without milk sample (Kala et al., 2019).

$$\% \text{ Protein} = (T2 - T3) \times 1.73$$

T2= Differences between 2nd and 1st titration readings.
T3= Blank titration reading.

Determination of acidity in milk samples

It determined using titrimetric method according to Association of Official Analytical Chemists (AOAC) procedure (Horwitz, 2000). The method is based on titration of lactic acid in the milk with a standard base (0.1 N NaOH), in the presence of phenol phthalein indicator.

$$\text{Lactic acid (\%)} = (9 \times V1 \times N) / V2$$

V1 = volume of NaOH standard required for titration.
N = normality of NaOH standard.
V2 = volume of milk taken for the test.

Determination of pH in milk samples

pH values were determined using pH portable meter (LaMotte 1741 pH Tracer PockeTester).

Results and Discusions

Detection of chemical adulterants in the milk samples

Results in table (2) presented that only four samples (M1, M2, M4 and M7) were positive in the NaCl test. Although one manufacturer (M4) has stated on the content

label (NaCl content is not exceed 0.1g/100 mL). However, according to the WHO recommendations it is considered as adulteration (Kirk et al., 1991).

Table (2). Results of detection of chemical adulterants.

No	Sample code	Starch Test	NaCl Test	$(NH_4)_2SO_4$ Test
1	M1	–(Negative)	+(Positive)	–
2	M2	–	+	–
3	M3	–	–	–
4	M4	–	+	–
5	M5	–	–	–
6	M6	–	–	–
7	M7	–	+	–

Detection of chemical adulterants in the milk samples.

Camel milk sample (M7) was the highest water content (90±0.612%) among other brands as showed in table (3) In addition, M7 was over the normal range according to USDA database in table (1-1), this might indicate there are added water in M7. While, M1 (88.40 ± 0.16%) and M2 (88.22 ± 0.51%) were just less than the normal range of raw milk (87.30–88.10).

In protein contents analysis; M3 (2.60±0.09%) was both less than the product label (3.2%) in table (4-1) and the normal range according to (US.FDA/CFSAN, 1998). In addition, M7 (1.38±0.17%) was less than the level (2.4–4.2%) according to USDA database. Some nutritional information (%) was found on products labels, they were as the table (4):

Table (3): Results of quantitative analysis of milk samples

Sample code	Water (%)	Acidity (%)	pH value	Protein (%)
M1	88.40 ± 0.16	0.169 ± 0.003	6.51±0.01	3.11 ± 0.17
M2	88.22 ± 0.51	0.179 ± 0.004	6.52 ± 0.01	3.46 ± 0.17
M3	86.94 ± 1.15	0.153 ± 0.009	6.56 ± 0.03	2.60 ± 0.09
M4	87.59 ± 0.28	0.210 ± 0.009	6.28 ± 0.03	3.63 ± 0.09
M5	87.09 ± 0.50	0.184 ± 0.005	6.4 ± 0.01	3.29 ± 0.09
M6	87.08 ± 1.35	0.186 ± 0.006	6.32 ± 0.04	3.29 ± 0.17
M7	90.00 ± 0.33	0.25 ± 0.004	6.11 ± 0.01	1.38 ± 0.17

All values = Mean ± Standard deviation for triplicate determinations (on different days)

Table 4: Nutritional information placed on products labels

Composition Label	M1	M2	M3	M4	M5	M6	M7
Protein content (%)	3	3.2	3.2	3.3	3.1	-	-

Titratable acidity and pH of milk analysis

In titratable acidity (TA) ; most of the samples were in the normal range according to FAO recommendations (0.10% –0.20%) (Draaiyer et al., 2009), except M4 (0.210±0.016%) and M7 (0.25±0.008 %) were significantly more than the normal range which may indicate that there are increasing in the production of lactic acid as a result of the bacterial growth according to FAO recommendations (FAO, 1986). In pH analysis; most of the samples were in the normal range (6.3-8.5) according to (US.FDA/CFSAN, 1998), except M4 (6.28 ± 0.05) and M7 (6.11 ± 0.03) were less than the normal range which support the result of the titratable acidity test. In addition, it supports the possibility that there is bacterial growth in M4 and M7.

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تحليل وكشف الغش التجاري لأنواع تجارية مختلفة من الحليب المتوفرة في السوق الليبي

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المستخلص

تعتبر مكافحة الغش التجاري ومراقبة جودة المنتجات الغذائية من الاهتمامات الدولية الرئيسية. لذلك استهدفت الدراسة تحليل 7 أصناف من الحليب التجاري المعروضة في السوق الليبي (مدينة اجدابيا) والتي أعطيت لها الرموز التالية: م1: ، م2: ، م3: ، م4: ، م5: ، م6: حليب ماعز محلي ، م7: حليب إبل محلي). تم إجراء ثلاثة تحاليل نوعية، وهي الكشف عن النشا وكلوريد الصوديوم وكبريتات الأمونيوم في المنتجات، وكانت النتائج سلبية باستثناء وجود كلوريد الصوديوم في م1 وم2 وم4 وم7. وكانت معظم النتائج في القيم المسموح بها باستثناء بعض العينات، ففي تحاليل محتوى الماء استنادا لقاعدة بيانات وزارة الزراعة الأمريكية، كانت نتائج م1 88.34±0.16% وم2(88.22±0.51%) أكثر بقليل من المعدل الطبيعي 87.3–88.1٪، بينما كانت في م7 90±0.33% فوق المعدل الطبيعي 88.7–89.4٪. في تحاليل محتوى البروتين كانت م3 2.60±0.09% أقل من مما هو مدون على علبة المنتج (3.2٪) وكذلك أقل من المعدل الطبيعي (2.4–4.2٪) وفقًا لقاعدة بيانات وزارة الزراعة الأمريكية، وأيضاً كان م7 1.38±0.17% أقل من المستوى. وفي تحاليل معايرة الحموضة كان م4 0.21±0.009%وم7 0.25±0.004% أعلى بكثير من الحد الطبيعي وفقًا لتوصيات منظمة الأغذية والزراعة(FAO) 0.10–0.20٪، مما قد يشير إلى وجود نمو بكتيري. بينما في تحاليل الرقم الهيدروجيني، كان م4 6.28±0.03 وم7 6.11± أقل من النطاق الطبيعي الذي يبلغ 6.3–) وفقًا لتوصيات إدارة الغذاء والدواء الأمريكية، وقد دعمت نتائج تحاليل الرقم الهيدروجيني أيضاً نتائج معايرة الحموضة. بشكل عام كانت نتائج عينة المنتج م7 الأسوأ مقارنة بباقي الانواع، لذلك على الجهات المحلية المخولة بمراقبة منتجات الألبان التأكيد على جودتها وسلامتها قبل وصولها إلى المستهلكين.

الكلمات المفتاحية: الغش، التحليل الكيميائي، السوق الليبي، الحليب.

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