The Quality Control of Some Sunscreen Products Selected From KSA Markets

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ABSTRACT: The current research aimed to assess the quality of twelve sunscreen products, all associated in the Saudi market. The study included several tests which were listed by The Saudi Standards, Metrology and Quality Organization. The following characteristics have investigated: visual inspection, thermal stability test at a certain temperature, pH, Bacterial (Microbiological) count test and water and total fats contents tests. There was a disparity in the results of trials, where many inexpensive samples failed to test the lipid content assessment, while most medium and expensive products exceeded all tests, which means they are desired and safe on the skin.

Keywords: HPLC-DAD, analysis, cosmetic control, Sunscreen, UV filters.

1. Introduction

Solar radiation has adverse effects on the exposed human skin. Amid all, UV is the greatest injurious. Unfortunately, measurements reveal on the last 20 years show that UV radiation which reaches the Earth's surface has risen by 6-14%[1]. Therefore it is imperative to protection from harmful UV lights. Ultraviolet (UV) light is partition within UVC (100–290 nm), UVB (290–320 nm), and UVA (320–400 nm)[2]. The growing awareness of the capabilities of sunlight to cause skin cancer and skin changes such as aging has resulted in a sharp increase in the sales of UV sun-protective products in recent years[3]. Sunscreen is a spray, gel, lotion or cream that reflects or absorbs some of the sun's UV radiation and protect the human skin against sunburn[4]. A frequency of use, applying method and storage conditions could profoundly affect the risk of microbial contamination of the products and a skin allergy[5].A lot of people do not now that each cosmetic product when uses on the skin produce a good rearing ground for bacteria, fungus, and microorganisms[6]. So, pH value must be on a certain degree that prevent the growth of Bactria and don't cause irritation of the skin. Creams shall be in the form of a thick emulsion or unctuous mass, with a pleasant odor, white or of uniform color. A small percent of fat cause the drying skin while the percent of water must be adjacent to protect the physical properties of cream as density and viscosity[7].

Correspondingly, the current research accomplished to the quality analysis of sunscreens products covering 12 popular brands available in KSA markets (imported from different countries) selected by consumer's voice. Sunscreens regulated by The Saudi Standards, Metrology and Quality Organization (SASO). To appraise the quality of searched sunscreen products accede to SASO, the following characteristics have examined: visual inspection, thermal stability test at a certain temperature, pH, Bacterial (Microbiological) count test and water and total fats contents tests.

2. Experimental

2.1 Sample collection and preparation

Many types and brands of sunscreen are available in the Saudi market. Twelve sunscreen products are chosen (are listed Table 1, they prices ranged from 8 to 221 SR ($2.14 - 58.67). Sample no. 7 (50 SR-13.35$ - no source inform) and sample no. 12 (221 SR- 59$ - France made) was the same brand, but one was imitation (no. 7) and another was original brand (no. 12). Samples have stored at room temperature in a suitable place.

2.2. Reagents and solutions:

Diethyl Ether (Techno Pharmchem, India), Distilled water (Milli-Q, France), Hydrochloric Acid 5N (BDH, UK), Magnesium Sulfate Anhydrous (Techno Pharmchem, India), Methanol HPLC grade (SIGMA-ALDRICH,Germany), Molecular Sieves (SIGMA-ALDRICH, USA) and Toluene (Riedel-de Haen, Germany).

2.3. Equipment's

Balance (Ohaus Corp., Pine Brook, NJ, USA), Hotplate stirrer (DaihanLabtech Co., LTD), Humidity chamber (JS Research Inc), Microscope (Omano OM88 1,600x Clinical Microscope), Oven (DaihanLabtech Co., LTD) and pH meter (Jenway, UK).

2.4. Methods of analysis:

The following tests were carried out according to GSO 1153/2010[8].

2.4.1 Visual inspection

The obtained Sunscreen Products accepted to a slip of organoleptic (color, smell, thickness) analyses.

- Procedure

The samples were visually examined by the naked eye to ensure compliance of the product with the SASO 1512/2002 [7].

2.4.2 Thermal stability test

Thermal stability is the fight of cosmetics to stable shift in properties passed by heat[9]. For thermal stability test Humidity chamber controlled at 60-70 %, relative humidity and a temperature of 37 ± 1oC used.

- Procedure

The samples placed on the inner surface of burning pipes and a 5 ml beakers that then placed for eight hours in the humidity chamber (again, at 37 ± 1 °C and 60-70% humidity). The samples were then removed from the chamber and checked for any separation of an oily layer. Thermal stability was considered to have demonstrated if no separation occurred[10].

2.4.3 Determination of pH value

pH can profoundly influence the effectiveness of a sunscreen chemical because of shifts in absorption characteristics[11]. An acidic solution considered as a solution has pH less than seven at 25℃, while the basic (alkaline) solution has pH higher than seven at the same degree of temperature [9]. The pH value shall be in the range of 5-9.5, according to the SASO 1512/2002 [7].

- Procedure

On 200-ml beaker, weight 10 ± 0.1 g of sample, add 90 ml of methanol. Heat the mixture at 45 °C and stir thoroughly for 15 min. The alcoholic layer was filtered and measure the pH value at 27°C.

2.4.4 Determination of the total content of fatty substance (TFS)

TFS: are essential characteristics decide the quality of sunscreen creams. The fatty substance is work to control the skin vernal and avoid the skin from gaining dry [9]. The total content of Fatty substance shall be not less than 15 % by mass, according to the SASO 1512/2002 [7].

- Procedure

Weigh 2 ± 0.1 g of cream in a 250 mL round flask and add 25-45 ml of hydrochloric acid (5 N). Add some pieces of the boiling regulator to the flask placed on the heater, then set the flask into the condenser and start the return heating of the cream for three hours or until the reaction mixture is clear. The content is poured into a 100 mL separating funnel and left to cool at room temperature. Rinse the ring beaker with 20 ml diethyl ether and then transfer to Suppression of separation. The water layer separated into a 250 ml cup, and the organic layer separated in a 250 ml cup after the extraction of the fat in the solvent three times. Wash the ether extract with 20 ml of distilled water twice inside the separating funnel and stir well to get rid of the acidic middle of the organic layer. Transfer the organic layer to the cup and place an appropriate amount of magnesium sulfate anhydrous and stir the mixture and then leave for 5-10 minutes (Rotary evaporator) and then filtration. The spatter is taken and returned to the round flask (known the weight). The ether then evaporates in the rotary evaporator, and then the beaker is weighed. Place the beaker in an oven to dry the fat at 60℃ for 10-20 minutes and weigh until the weight set[10].

- Calculation

Total content of fatty substance, % by mass = 100 xW1 / W2 --- Equation(1) for calculate TFS

Where:

W1 = mass of the residue, g.

W2 = mass of the test sample, g.

2.4.5 Determination of water content

The water content influences the physical properties of a product including weight, density, viscosity, and refractive index. Water is required for the proper mixing of all the constituents and also to prevent the skin from getting dry [9]. The water content shall be not more than 85 % by mass, according to the SASO 1512/2002 [7].

- Procedure

It weighs 2.5 g of cream into a 250 mL round flask and adds 25 mL of toluene (after drying it with Molecular Sieves). Add pieces of the boiling regulator to the flask and then put the flask on the heater, Where the water trap tube that connected to the condenser installed on it and the bottom of the water trap tube filled with toluene. Cover the round beaker with glass wool and tin and cover the cotton and tin reception tube. A heater heats the flask until the reaction mixture begins to boil and the water droplets begin to fall into the trap tube, and the heating continues. Note that the amount of water is constant after some time (30-60 minutes) in the

trap tube and this means the completion of water extraction from the cream. The internal surface of the condenser is washed by toluene to remove any trace of water and stops heating and leaves the trap tube to cool. The water separated from the toluene by removing it from the valve switch with the trap tube and then measuring the water volume[10].

- Calculation

Water content, % by mass = V xd x100 / W ---- Equation(2) for calculate water content

Where

V = volume of water, ml

d = density of water

W = mass of the test sample, (g)

2.4.6 Bacterial (Microbiological) count test

Excessive amounts of bacteria and fungus can affect the cosmetic in many ways; cause odors, destabilize the emulsion, cause color changes. Microorganisms can also affect the consumer negatively in styles ranging from harmless itching of the skin to severe infection; even blindness if the product used around the eyes[6].The maximum micro-organism number per gram for Sunscreens is 100 /g according to the SASO 1512/2002 [7].

- Procedure:

This experiment was designed to assess the count of collected bacteria present in the sample in Petri dishes. The plates were incubated at 37°C for 24h after isolation from the sample. Researchers have evaluated the visible colonies using an Inter science Scan 500 colony counter. Further, they counted bacterial colonies in CFU/g and made a comparison with the control[12].

3. Result and Discussions

3.1 Visual inspection

It shall be in the form of a thick emulsion or unctuous mass, with a pleasant odor, white or of uniform color [7] — results in Table 2.

It has noticed that all samples have a homogeneous aspect and a specific smell according to the SASO 1512/2002 specification. Noted that, samples 7 and 12 showed the same result.

3.2 Thermal stability test

Consequently to the stability test on 37 ± 1°C and humidity of 60 - 70% for 8h it has concluded that all the analyzed products are acceptable according to the SASO 1512/2002 specification, none show any separation and are thermally stable. Results in Table 3.

3.3 Determination of pH value

Monitoring the pH value is crucial for determining the products' stability. pH changes indicate the occurrence of chemical reactions that can give an idea about the quality of the final product. The pH of human skin ranges typically from 4.5 to 6.0 [13]. Therefore, for a formulation to possibly gain admission for industrial application, it should have a pH that is included in this range or close to it in the field of 5-9.5 according to the SASO 1512/2002. All products in this work had a pH value within the specified range, implying that they were safe for application on the skin. The results of pH shown in Table 3 (Fig. 1). Sample 11 (5.30) has the lowest pH value and sample 10 (8.12) the highest. While the results of pH for the samples 7 and 12 a very close, 6.80 and 6.82 respectively.

3.4 Determination of the total content of fatty substance (TFS)

Most products in this work had a TFS value above the minimum requirement of 15% according to the SASO 1512/2002 specification. But five value is lower than 15% (samples 1, 2, 3, 5, 10). The results of the TFS values shown in Table 3 and (Fig. 2).

By comparing the ratio of fatty content in samples 2, 3 and 5, which contains the least amount of fat (5.09, 3.94, 2.14) respectively with the information on the packaging, it found that these samples written on their packages sunblock. It also observed that sample 12 and sample 7 replicates in the brand had a large proportion and Converged of fat (51.25, 56.77) respectively.

3.5 Determination of water content

The test results show that a significant part of the sunscreen creams is water content, varying from 16 percent to 67 percent. All samples are acceptable according to the Saudi Standard requirement SASO 1512/2002. The results of water content shown in Table 3 and (Fig. 3).

Considering the water percentage

- It found that the samples containing a high percentage of water are the cheap samples (1, 3, 4 and 5) except sample 2, by reference to the ingredients written on the packaging of these samples found that the water in the top ingredients of the cod on the packaging to samples (1, 3, 4 and 5), while it found that water is the last component written on the sample package 2, where writes the highest components concentration first and then less and less.
- It noted that deluxe samples (10, 11 and 12) contained the lowest percentage of water. It was the sample 12, and sample 7 replicates in the brand had a small percentage of water and were also converging.

3.6 Bacterial (Microbiological) count test

The maximum limit in sunscreens is 100 CFU/g according to SASO. The results of the microbiological examination are compatible with the permissible limits of SASO 1512/2002. Registered sample 2 with the highest value 58.5 CFU/g, while sample 8 has the lowest value of bacteria account 19. Table 3 shows the average value of the bacterial count of the samples (Fig. 4).

A study suggested in 2013, the combination of benzophenone-3, octyl, and titanium dioxide be exciting since it preserved physicochemical properties of the product and was efficient against the growth of different spoilage microorganisms [13].

We have two samples (4-9) containing these ingredients, already it preserved physicochemical properties of the product and had low microbial count values.

It also observed that sample 12 and sample 7 replicates in the brand are had a low proportion of bacteria (23, 29.5) respectively, but sample 12 (original product) has the lowest value 23 CFU/g. The bacteria account decreased with increasing the price of products.

3-7 Comparison between the current study results and the results of literature review:

Comparing our results to SASO tests with the results of many types of research conducted in different countries (India, Thailand, Pakistan, Romania, and Tunisia) on different cosmetics, that found the results obtained are consistent with most of the results of these researches Table 4.

All studies results are Satisfactory as a current study on visual inspection, thermal stability, pH values, and bacterial count tests. Only India study on herbal lotions was found them false on TFS and water contents tests. Current study successive all samples on all tests except five products which false on TFS test, may be due them low prices. So, people must wear when using herbal and inexpensive products.

4. Conclusion:

The findings presented in the current study indicated on twelve samples under-investigated research seven of them pass succeeding all experiments (4, 6, 7, 8, 9, 11, 12). They cast ranged from medium to high prices. While five samples (1, 2, 3, 4, 5, 10) were a defeat on TFS test, so SASO will ban them from selling on Saudi markets. Consuming these products will case the dryness of skin consumers, as a result of a small percentage of fat, while the skin needs to dabbling. Sample seven was replicate of sample twelve (all France made), they have close results of tests, that indicate the closer on compositions of two products, but an expensive one (sample 12) has less of bacteria count.

The analytical procedures successfully applied to the commercial samples and easy to implement in quality control contexts within the cosmetics industry as part of the effort to ensure that commercially available products adhere to regulatory standards, which in Saudi Arabia are established by the SASO. Given the potential health risks associated with both UV radiation and the products used to protect against it, regulatory authorities must be vigilant about employing the best available quality controls and screening as should indeed be the case for all products designed to come into direct and long-term contact with the skin, and especially those that are imported. Consumers for their part must be not covetous themselves to buy the best products even at a high price. Also, they must be advice cosmetic expert or doctor on dermatology before purchasing the products.

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Table 1: Sample collection

Sample	SPF	Country	Price ($)
1	-	Indonesia	2.67
2	15	Philippines	2.67
3	25	Thailand	2.13
4	20	Philippines	2.67
5	45	USA	5.33
6	50+	Spain	10.66
7	-	-	13.33
8	30+	Lebanon	16
9	50+	Italy	14.66
10	30	-	24
11	100	FRANCE	26.66
12	30	FRANCE	58.92

SPF: number refers to the product's ability to block out harmful radiation

Table 2: The organoleptic characteristics of Sunscreen products.

Samples	Color	Smell	Thickness	Diacritics with SASO specification
1	light pink	Acceptable	Creamy medium	Approving
2	White	Acceptable	Creamy medium	Approving
3	White	Acceptable	Creamy light	Approving
4	yellowish white	Acceptable	Creamy thick	Approving
5	White	Acceptable	Creamy medium	Approving
6	yellow	Acceptable	Thick emulsion	Approving
7	Pink whitener	Pleasant odor	Creamy medium	Approving
8	White	Pleasant odor	Thick emulsion	Approving
9	yellowish white	Pleasant odor	Creamy light	Approving
10	White	Pleasant odor	Thick emulsion	Approving
11	White	Acceptable	Thick emulsion	Approving
12	Pink whitener	Pleasant odor	Creamy medium	Approving

Table 3: The results of pH, TFS, Water content and Bacterial count for sunscreen products.

Sample	Test / Permitted limits			
	pH (at27°C ± 2°C) 5-9.5	TFS higher than15%	Water content Less than 85%	Bacterial count Less than100 CFU/g
1	6.79±0.46	10.51±0.69+	52 ± 0	48 ± 2.8
2	7.09±0.22	5.09±0.10+	39 ± 1.4	58.5 ± 2.1
3	6.60±0.17	3.94±0.27+	67± 1.4	37 ± 0.2
4	7.13±0.29	59.60±0.57	51 ± 1.4	37.5 ± 0.7
5	6.12±0.08	2.14±0.07+	67 ± 1.4	29 ± 2.8
6	6.95±0.35	22.91±0.70	24 ± 0	33.5 ± 0.1
7	6.80±0.39	51.25±1.00	16 ± 0	29.5 ± 2.1
8	6.58±0.15	53.25±0.99	47 ± 1.4	19 ± 2.8
9	6.64±0.06	30.42±0.65	35 ±1.4	26 ± 0.2
10	8.12±0.11	10.01±1.00+	19 ± 1.4	31 ± 1.4
11	5.30±0.25	28.43±0.18	20 ± 0	21.5 ± 0.7
12	6.82±0.50	56.77±0.30	17± 1.4	23 ±1.4

- No. of determinations: 3
- + The result no approving with SASO

Table 4: Comparing between our results to SASO tests with the results of a number of researches conducted in different countries on different cosmetics.

Country	Cosmetics	Visual inspection	Thermal Stability	pH	TFS	Water content	Bacterial count	References
KSA	12Sunscreens	Ok	Stable, no oil separation	5-8	2-60%	16-67%	19-58.5	This study
India	2 Herbal lotion	Ok	Stable, no oil separation	About 7	12.5%	88%	Satisfactory	[14]
Thailand	2 Sunscreens	Ok	–	6-8	–	–	–	[15]
Pakistan	2 Creams	–	Stable, no oil separation	5-6	–	–	–	[16]
Romania	3 Dermo-cosmetic products	Ok	–	5-6	–	50-72%	Satisfactory	[17]
Tunisia	4 Sunscreen	Ok	Stable, no oil separation	About 6	–	–	Satisfactory	[13]

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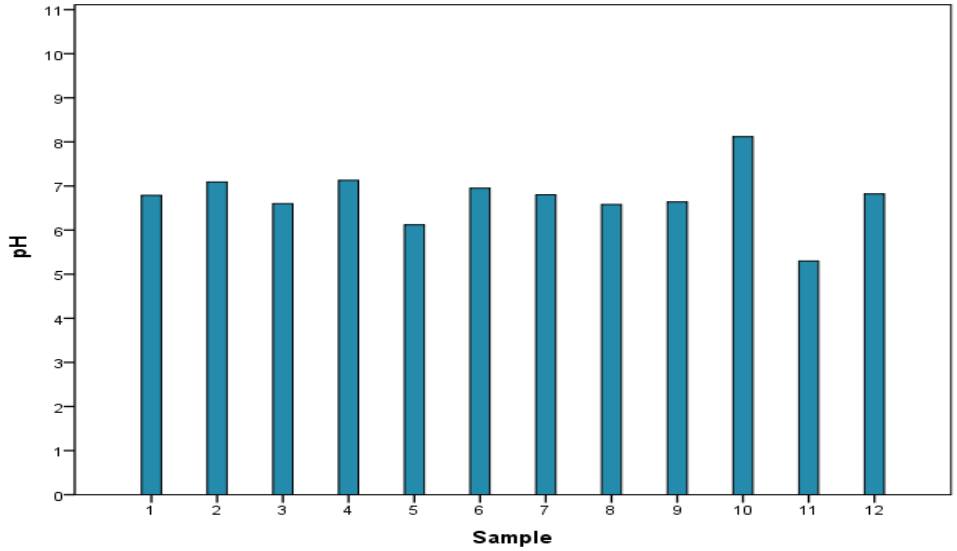

Figure 1: The average value of pH measures of the samples.

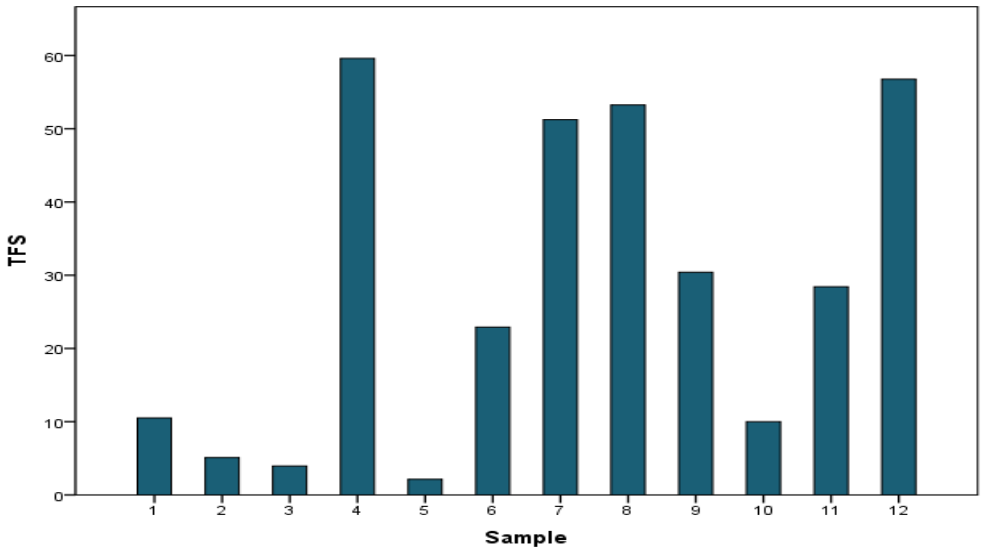

Figure 2: The average value of TFS of the samples

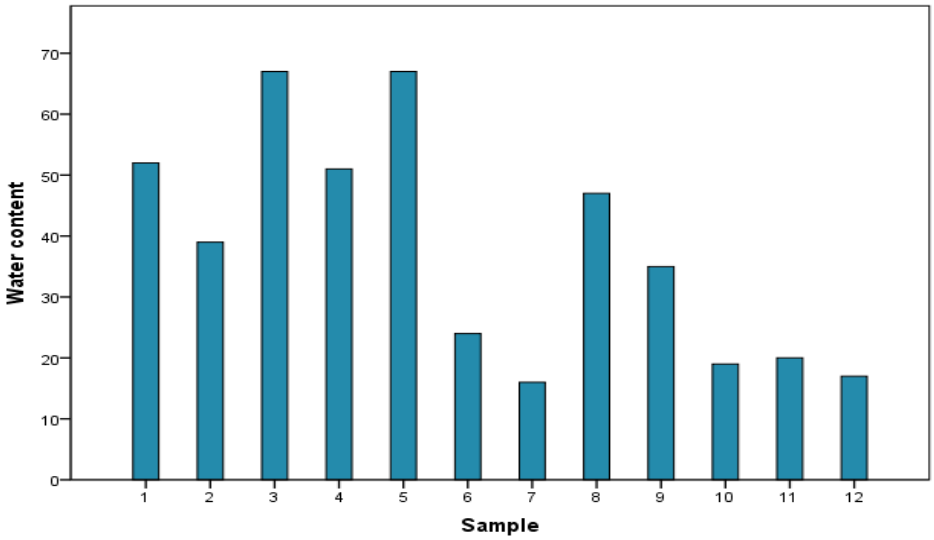

Figure 3: The average value of water content of the samples

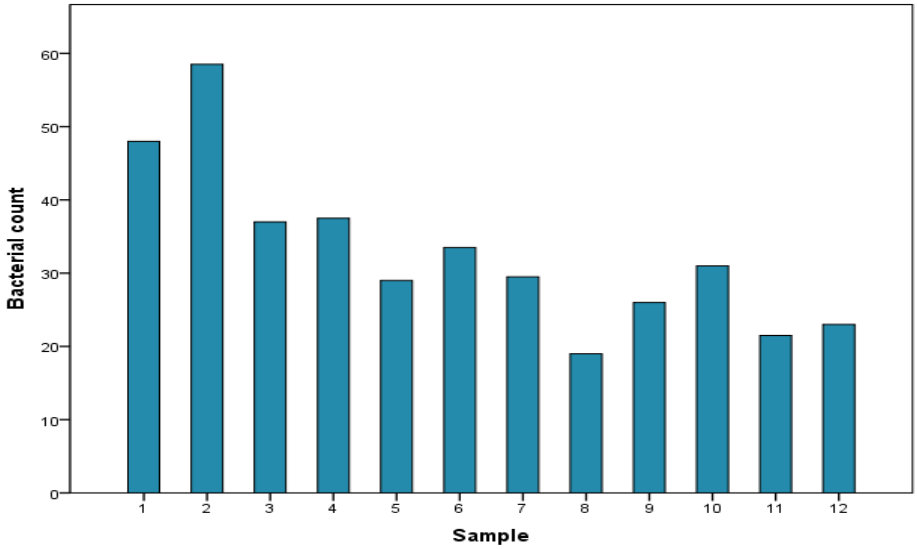

Figure 4: The average value of the Bacterial count of the samples.