Exploration on key factors for overall migration into olive oil of food-contact silicone

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Abstract. To ensure the accuracy of the overall migration into olive oil of high risk food-contact silicone products, the key factors of the test method on the base of EN1186-1 & 2 were analyzed and discussed. Two sample conditioning methods for the silicone products were compared, and the extraction times for olive oil in the samples were investigated, as well as the change trend of the actual temperature of olive oil at the set temperature. Using calcium chloride dryer conditioning method can achieve the same effect of constant temperature and humidity method, and can significantly reduce the conditioning time. For silicone products that are easily absorbed oil, the olive oil in the sample should be extracted at least twice. The temperature of the oven should be increased appropriately to meet the requirements of the temperature of olive oil. The water conditioning of samples, the extraction times of olive oil and the preheating temperature of olive oil are the key factors for olive oil overall migration of food-contact silicone, which can provide a reference for testing workers of food-contact materials.

1. Introduction

Silicone rubber material is commonly used in food-contact materials because of its unique advantages, such as baby feeding equipment, baking tray, cake mold and other baking equipment, steaming mats, spatula and other kitchen utensils. However, silicone rubber products in the processing process, the use of organic dyes, vulcanization accelerator, antioxidants, anti-aging agents and other additives. Therefore, some toxic and harmful additives and unintended additives may migrate from silicone rubber products to food, bringing safety risks [1-3]. SVHC in food contact silicone products, including phenols, anilines, organotin, siloxane, aliphatic aldehydes and thiazoles have been detected [4-8]. Therefore, silicone rubber products belong to food-contact high risk materials and is required to be strictly tested.

SN/T 2334-2009 Food contact material-Test methods for overall migration into olive oil-Total immersion [9] and other methods have been included in the entry and exit standards in China. European Union and other countries have a series of standards such as EN1186-1&2-2002 Test methods for total immersion of materials and articles in contact with food-stuffs-Plastics, total migration to olive oil [10,11]. In practical work, it was found that there were problems in the implementation of the test of total migration of olive oil in food-contact silicone products, such as there were many kinds of contact materials in food-contact oil without specific directions, harsh water conditioning of samples, and uncertain extraction times of olive oil in samples [12,13].

In this study, food-contact silicone products, which is easy to absorb water and oil, was selected as the sample on the basis of EU standard EN1186-1&2. In order to improve the accuracy of the test results
of overall migration into olive oil of high risk food-contact silicone products, several key factors in the test process were experimented and discussed. It is expected to provide some reference for domestic laboratory workers in the detection of food contact materials.

2. Materials and Methods

2.1. Materials and reagents
Heptadecanoic acid triglyceride (purity 99.9%, Shanghai Anpu Experimental Technology Co., Ltd.); Olive oil (Chemical Pure, Shanghai Sinopharm Group); Ethanol, sodium chloride, potassium carbonate, calcium chloride (analytical purity, Guangzhou Chemical Reagent Factory), n-heptane, cyclohexane, saturated sodium sulfate solution, mixed solution of boron trifluoride and methanol (analytical pure, Tianjin Zhiyuan Chemical Reagent Co., Ltd.).

The test sample was commercially available silicone in baking biscuit molds.

2.2. Instrument
7890B-7693A gas chromatography (with hydrogen flame ion detector, Agilent, Inc., USA); B-811 automatic Soxhlet extractor (Buchi, Switzerland); Rotary evaporator (Jinan Olebo, Shandong); Electronic balance (MS204S, Shanghai Mettler Toledo Instrument Co., Ltd.); Thermocouple, temperature and humidity meter (Dongguan Wanchuang Electronic Products Co., Ltd.); Magnetic agitator (Shanghai Anpu Experimental Technology Co., Ltd.)

2.3. Methods
According to EN1186-1&2, the sample area of 10 cm x 10 cm was accurately cut, and then evenly cut into 3 pieces. The sample was put into a dryer for conditioning. Then weighed the sample Ma. The prepared sample is immersed in the olive oil that has been preheated to the test temperature. After soaking, removed the sample from the olive oil, and wiped the olive oil adhered to the sample surface with industrial wipe paper, continued to dry in the dryer, and registered the drying quality of the sample Mb.

Next, the weighed samples added 200 mL n-pentane and 10 mL internal standard cyclohexane solutions to extract by Soxhlet. After extraction, concentrated the extract until the solvent evaporates completely with rotary evaporator. Following, added 10 mL n-heptane and 10 mL potassium hydroxide methanol solutions to the concentrated solution, then heated and refluxed for (10 ± 1.0) min. After cooling, 5 mL boron trifluoride methanol solutions were added, heated and refluxes for (2 ± 0.25) min. Cooling to room temperature, added 15 mL saturated sodium sulfate solution for 1.5 h, and then taked the supernatant for GC-FID analysis.

2.4. Analysis conditions of gas chromatography
The chromatographic column: DB-WAX, 30m×0.25mm×0.25μm. Carrier gas: helium, 99.99% purity. Sampling method: shunt ratio 10:1. Injection volume: 1 μL. Inlet temperature: 220℃. Heating procedure: the initial temperature is 140℃, 1min, 5℃/min to 190℃, and the temperature is maintained for 14 min. Flow rate of hydrogen: 30 mL/min, air flow rate: 300mL/min, FID temperature: 240℃.

2.5. Sample conditioning method
Constant temperature and humidity conditioning method: six samples were placed in a container of 20±2℃ and 50±10% relative humidity, and weighed every 24±2h, until the mass change is less than 2 mg, record the constant mass Ma1. Calcium chloride dryer conditioning method: six samples were placed in the calcium chloride dryer container, and weighed every 6±1h, until the mass change is less than 2 mg, record the constant mass Ma2.
Next, soaked the sample in the preheated olive oil at 70℃ for 2 h, removed the oil from the surface. And then, the samples were used the corresponding sample conditioning, until the mass difference between two times is less than 2 mg, and record the constant mass MB1 and MB2, respectively. Samples before and after soaking olive oil quality differences for | Ma - Mb |.

2.6. Extraction method of olive oil from samples
The first extraction method: six samples were cut and dried. Then soaked in preheated olive oil for 70℃/2 h. And then analyzed the quality of olive oil in the sample after the first extraction according to 2.3. The second extraction method: keep the first sample in the Soxhlet extraction tube, add 200 mL anhydrous ether and add 10 mL of internal standard-cyclohexane solution for second Soxhlet extraction for 7 h. And then analyzed the quality of olive oil in the sample for extraction according to 2.3.

The quantitative analysis of the quality of olive oil absorbed by the sample were the same as that of reference [14].

2.7. Actual temperature test of olive oil at set temperature
50 ml olive oil was put into 100 ml iodine flasks, and the oven temperature was set at 40℃, 70℃, 100℃ and 175℃, respectively. Meanwhile, the actual temperature of olive oil was compared on the oven temperature at 41℃, 72℃, 105 and 185℃, respectively. The actual temperature of olive oil was measured by thermocouple every 60 min, and three parallel samples were made for each temperature condition.

3. Results and discussion

3.1. Comparison of sample conditioning methods
The main purpose of sample conditioning is to keep the water of the sample consistent before and after soaking olive oil. Sun[15] also concluded that the test results of water sensitive samples without conditioning were significantly higher than those after vacuum drying, resulting in false positive results. Therefore, sample conditioning must be carried out when detection on overall migration into olive oil for moisture sensitive samples.

However, in practical work, constant temperature and humidity conditioning method according to the standard, the temperature and humidity control requirements for sample conditioning are very harsh, and it takes a long time for a sample to reach a constant weight. Therefore, this experiment tried the calcium chloride dryer conditioning method, and compared with the constant temperature and humidity method.

The experimental results show that the constant weight requirement <2 mg (0.002 g) can be achieved when placed in 20±2℃, 50±10% constant temperature and humidity environment for at least 72 hours. While using calcium chloride dryer with stronger water absorption for sample conditioning, the constant weight requirement can be reached in 12 hours (see Table 1).

The quality changes of samples before and after soaking olive oil by the two sample conditioning methods were compared, and the results were shown in Table 2 and Table 3 below. The results showed that the average quality changes of the samples before and after soaking in olive oil were basically close, and there was no significant difference. Therefore, the calcium chloride dryer conditioning for silicone products can quickly reach constant weight, which conditioning time was shortened from 72 h by constant temperature and humidity conditioning to 12 h.
Table 1 Comparison of the time required for sample to constant weight by sample conditioning

| Sample conditioning methods | Sample quality difference |
|-----------------------------|---------------------------|
| 48 h, Ma\textsubscript{48h}-Ma\textsubscript{48h} (g) | 0.022 0.026 0.021 0.018 0.023 0.024 |
| 72h, Ma\textsubscript{48h}-Ma\textsubscript{72h} (g) | 0.000 0.001 0.000 0.000 0.000 0.000 |
| 6 h, Ma\textsubscript{0h}-Ma\textsubscript{6h} (g) | 0.032 0.033 0.031 0.031 0.030 0.031 |
| 12 h, Ma\textsubscript{6h}-Ma\textsubscript{12h} (g) | 0.001 0.001 0.000 0.001 0.000 0.001 |

Table 2 Quality changes of samples before and after soaking olive oil by constant temperature and humidity conditioning

| Sample quality | 1 2 3 4 5 6 Average (g) |
|----------------|------------------------|
| Ma\textsubscript{2} (g) | 43.9529 38.2285 41.5495 39.1441 39.6917 42.5295 |
| Mb\textsubscript{2} (g) | 43.9794 38.2564 41.5756 39.1717 39.7184 42.5565 |
| | | 0.0265 0.0279 0.0261 0.0276 0.0267 0.0270 |

Table 3 Quality changes of samples before and after soaking olive oil by calcium chloride dryer conditioning

| Sample quality | 1 2 3 4 5 6 Average (g) |
|----------------|------------------------|
| Ma\textsubscript{2} (g) | 40.6014 39.9786 39.4977 38.7181 39.2000 39.0232 |
| Mb\textsubscript{2} (g) | 40.6290 40.0051 39.5247 38.7452 39.2261 39.0490 |
| | | 0.0276 0.0265 0.0270 0.0271 0.0261 0.0258 |

3.2. Extractions times for olive oil in the sample

Compared with the quality test data of olive oil after extraction with n-pentane for one time and diethyl ether for 2 times, it was found that a small amount of olive oil could be detected in the samples after the second extraction. The standard deviation of the quality of olive oil in the samples after extractions for one time and 2 times was 1.43% and 0.66%, respectively, as showed in Table 4. Therefore, for silicone samples with loose texture that absorb more olive oil, it is necessary to extract the olive oil in the
samples at least twice.

The experimental results of Sun Wenwen[14] also mentioned that, when testing the total migration of olive oil, different matrix materials have unique structure densities and different absorption degrees of olive oil. In order to obtain a more accurate, the material that absorbed more olive oil must be further extracted with ethyl ether (second extraction) until the olive oil is completely extracted, while olive oil quality is more than 10 mg of samples. Therefore, the extraction times of olive oil in samples should be judged according to the material of samples. It is suggested that each laboratory establish a sample database to provide technical guidance for laboratory workers on food contact materials.

Table 4 Quality changes of olive oil by two extraction samples

| Olive oil quality | 1   | 2   | 3   | 4   | 5   | 6   | Average (g) | STD(%) |
|-------------------|-----|-----|-----|-----|-----|-----|-------------|--------|
| First extraction,Mc1 (g) | 0.1845 | 0.1904 | 0.1865 | 0.1928 | 0.1878 | 0.1857 | 0.1812 | 1.43   |
| Second extraction,Mc2 (g) | 0.0315 | 0.0091 | 0.0285 | 0.0145 | 0.0227 | 0.0308 | -         | -      |
| Total Mc (g)       | 0.2160 | 0.1995 | 0.2150 | 0.2073 | 0.2105 | 0.2165 | 0.2108 | 0.66   |

3.3. The actual temperature trend of olive oil at the set temperature

The actual temperature of olive oil at the set temperature of oven is shown in Fig. 1a-d. When the oven temperature was set at 40 °C, 70 °C, 100 °C and 175 °C, the actual temperature range of olive oil (three parallel samples) was 38 °C~ 39 °C, 65 °C~ 68 °C, 91 °C~ 95 °C and 165 °C ~ 168 °C respectively, after 2 ~ 3 h preheating. Therefore, it could not meet the requirements of olive oil temperature range 40 ± 1 °C, 70 ± 2 °C, 100 ± 3 °C, 175 ± 5 °C. When the oven temperature was raised to 41 °C, 72 °C, 105 °C and 185 °C, the actual temperature range of olive oil could reach 40 °C ~ 41 °C, 70 °C ~ 72 °C, 100 °C ~ 102 °C and 170 °C ~ 175 °C after 2 hours., which could meet the standard requirements. Therefore, the temperature of the oven needs to be appropriately increased, and the actual temperature of olive oil could meet the standard after 2 hours in the detection process.
b. Oven temperature at 72°C

C. Oven temperature at 70°C

D. Oven temperature at 72°C

E. Oven temperature at 100°C

F. Oven temperature at 105°C
Fig. 1 Trend of olive oil temperature with time at different oven temperatures. 40°C (A), 41°C (B), 70°C (C), 72°C (D), 100°C (E), 105°C (F), 175°C (G), 185°C (H)

4. Conclusion
This study aims at the problems encountered in overall migration test of silicone products, which are easy to absorb water and oil. The method of moisture conditioning with calcium chloride dryer can achieve the effect of constant temperature and humidity conditioning to constant weight of samples, and can also shorten the conditioning time to 12 h. The extraction times of olive oil in the samples were investigated. It showed that the olive oil in the samples was extracted at least twice for the silicone products that absorb more olive oil. And the relative deviation of olive oil quality in parallel samples was reduced from 1.43% to 0.66%. To compare the temperature change of olive oil under the set temperature, the oven temperature should be raised to 41°C, 72°C, 105°C and 185°C respectively. Then the immersion temperature of olive oil specified in the standard can be 40 ± 1°C, 70 ± 2°C, 100 ± 3°C, 175 ± 5°C after 2 hours of preheating. This study serves as a reference for improving the accuracy of overall migration detection of food contact materials in olive oil.

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