



# Analysis of potential migration compounds from silicone molds for food contact by SPME-GC-MS

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## ABSTRACT

Four commercially available silicone cupcake molds have been studied. An evaluation of the post-cure treatment applied to the silicone molds was carried out and the loss of volatile organic compounds after cure treatment was quantified. The two higher quality molds showed losses at the 0.5% (w/w) (recommended by BfR standard), while the two lower quality molds exceeded this limit.

The migration studies were carried out using Tenax® as a solid food simulant. The volatile compounds that migrate were identified and quantified using SPME-GC-MS. Up to fourteen silicone oligomers were quantified. When the molds were subjected to post-cure treatment, none of them exceeded the global migration of 10 mg/dm<sup>2</sup>; while those lower quality molds showed migrations higher than 10 mg/dm<sup>2</sup>, so their use in contact with food is not recommended.

## 1. Introduction

Currently, there is a return to the preparation of home baking, thus taking out the more creative side to prepare dishes and desserts with products from the pantry. Among the categories that have grown the most in sales in recent years are that related to baking ingredients and kitchen utensils.

The use of silicone molds offers the following advantages: ease of removing the baked food from the inside of the mold, since the material does not retain much heat and prevents possible burns when handling it; recovery of the initial shape after use, which allows its reuse for a long time; diversity in sizes, shapes and colours that makes it very attractive commercially; as well as versatility in its use both for conventional ovens, microwave ovens and/or freezers. The main function of these molds is to contain the product to be baked/frozen so that the final product acquires the characteristic shape of the mold and prevent it from being lost or contaminated with the outside.

Helling et al. (2009) observed that silicone elastomers (amorphous polymers) are not totally inert when they come into contact with fatty or oily food and can sometimes show high migration compared to metal molds. In addition, there is the possibility that siloxanes are formed during the use of silicone products, for example, by repeated use of the baking pan at high temperatures (Cederberg and Krüger, 2017).

Therefore, after being manufactured, all silicone products that are to be used in contact with food should undergo a heat treatment called post-curing, which consists of heating at 200 °C for at least 4 h. This way, the amount of low molecular weight siloxanes (VOCs: volatile organic compounds) present in the product is reduced and can be released and come into contact with food when used at high temperatures. This heat treatment is necessary to meet the requirements according to the Bundesinstitut für Risikobewertung (BfR standard, 2007) "Recommendations on Food Contact Materials", a German standard that is not mandatory, which establishes that there should not be losses greater than 0.5% (w/w) in materials intended for contact with food, after the aforementioned post-curing treatment.

An important aspect to study and control is the possible packaging/food migration that silicone molds may present as a result of heating at high temperature, which can cause alterations in the composition of the food and its organoleptic characteristics. Being materials that are in direct contact with food, it is important to check that they do not release compounds that are harmful to the health of consumers.

Royal Decree 847, 2011 in accordance with Regulation No 1935, 2004, establishes the rules and the limits for some materials and objects which are not yet covered by the EU legislation, such as adhesives; natural and synthetic elastomers and rubbers; ion exchange resins; silicones and varnishes; coatings; and plastic materials not included in

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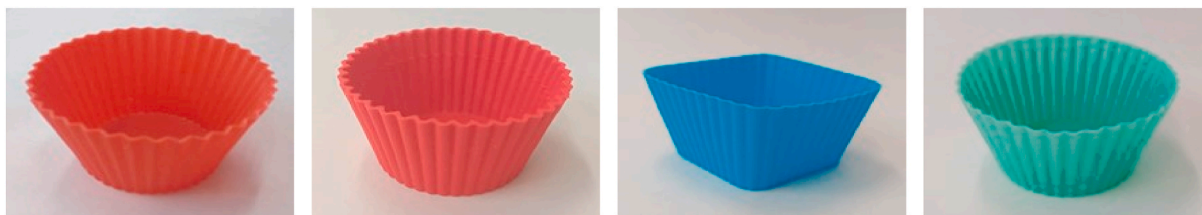


Fig. 1. Studied silicone molds (L, S, C and CC). (use colour). (For interpretation of the references to colour in this figure legend, the reader is referred to the Web version of this article.)



Fig. 2. Hermetically sealed jars where migration tests were carried out. (use colour). (For interpretation of the references to colour in this figure legend, the reader is referred to the Web version of this article.)

Annex I of Regulation No 10, 2011 (AESAN, 2020).

Recent studies show the identification of non-volatile migrants by UPLC-Q-TOF-MS in baby bottles (da Silva-Oliveira et al., 2019) and from kitchenware utensils to food (Canellas et al., 2021); as well as the use of HS-SPME-GC-MS for the identification of odorants in baby bottles (da Silva-Oliveira et al., 2020). In this work, SPME-GC-MS solid phase microextraction has been selected as a technique for analysing volatile migrating compounds in order to identify and quantify the silicone oligomers and other compounds that migrate from the silicone cupcake molds under study.

## 2. Materials and methods

### 2.1. Chemicals and analytical standards

Octamethylcyclotetrasiloxane (556-67-2) decamethylcyclopentasiloxane (541-02-6), dodecamethylcyclohexasiloxane (540-97-6), butylated hydroxytoluene (128-37-0), hexadecanoic acid (75-10-3), 2,6-diisopropyl-naphthalene (24157-81-1) and hexadecanoic acid, methyl ester (112-39-0) used as analytical standards for quantification were from Sigma-Aldrich (Spain). Ethanol from Scharlab (Madrid, Spain), sodium chloride from Panreac (Barcelona, Spain) and poly (2,6-diphenyl-p-phenylene oxide) polymer (Tenax®) supplied by Supelco (Vidra Foc, Spain) were used.

The stock solutions of the analytical standards used were prepared at concentrations approximately 1000 µg/g in absolute HPLC-grade ethanol. All of them were subjected to gravimetric control. From the stock solutions, the corresponding dilutions of the calibration curves were prepared at 20% ethanol with deionized water. These solutions were injected into the SPME-GC-MS equipment within a maximum of 24 h after their preparation.

### 2.2. Samples

To carry out this study, four silicone cupcake molds were selected

among the two qualities that can be found in the Spanish market. Two silicone molds were selected from manufacturers that certify the quality of the product and that have a much higher cost for the consumer who buys them, which were called L and S molds. Their specifications ensure that they are made from platinum silicone and that each mold has undergone a heat treatment of between 6 and 7 h to eliminate potentially toxic residues. On the other hand, two molds were selected from lower quality manufacturers, with a significantly lower price, of which the manufacturer does not report their characteristics, only present the European stamp for being used in contact with food (Regulation (EC) No 1935/2004), and which were called C and CC molds. Fig. 1 shows the four silicone molds under study.

### 2.3. Post-cure treatment study

When using silicone molds at high temperature in an oven up to 220 °C, it is important to check that the weight loss is less than 0.5% when heated to 200 °C, for at least 4 h (BfR standard, 2007) in order to ensure that the volatile compounds that can be released (VOCs), when silicone molds are used for the first time, are not harmful to the health of consumers.

Therefore, the first thing that was done with the four molds under study was to analyse the weight loss after heating at 200 °C with a temperature control of ±1 °C for 4 h, in correlation with current studies with silicone molds, where they applied this heating period to the silicone, in order to evaluate the post-curing treatment applied to the material (da Silva-Oliveira et al., 2020). The procedure consisted of first, having the molds in a desiccator with calcium chloride (CaCl<sub>2</sub>) for 96 h, then weighing the molds and immediately put them in an oven at 200 °C for 4 h (Mettmert Universal oven UF110, Mettmert GmbH + Co. KG). After the time set, the molds were again put in the desiccator for 96 h and finally weighed again on an analytical balance, recording weight loss produced.

**Table 1**  
Results obtained after applied post-curing treatment to silicone molds.

Sample	Weight before (g)	Weight after (g)	Loss(g)	% Loss	% Mean
L1	8.0209	7.9913	0.0296	0.37	0.35
L2	8.7123	8.6835	0.0288	0.33	
S1	13.0392	13.0100	0.0292	0.22	0.23
S2	13.0653	13.0339	0.0314	0.24	
C1	6.9781	6.8350	0.1431	2.05	1.98
C2	6.9023	6.7708	0.0915	1.91	
CC1	8.0783	7.9786	0.0997	1.23	1.22
CC2	8.8142	8.7074	0.1068	1.21	

## 2.4. Migration study

To evaluate the use of these silicone molds at high temperature, the procedure described in Regulation (EU) No. 10/2011 for these migration studies was followed. In Royal Decree 847/2011, applicable to silicones, it is stated that migration tests may be carried out either on food products or simulants, and that the tests to check whether migration to food products is within the maximum limits allowed will be made in the most extreme conditions of duration and temperature foreseeable of real use.

In this work, silicone molds for baking cupcakes (dry food) have been studied. The regulation determines that the simulant to be used must be simulant E. This simulant is a poly (2,6-diphenyl-p-phenylene oxide) polymer also called Tenax®.

Before its use in migration tests, the Tenax® must be previously cleaned by Soxhlet extraction with acetone for 6 h, as described in [Standard UNE-EN 14338](#). In addition, following this same standard, the amount of simulant E was calculated (g) to be used in each test based on the contact surface (dm<sup>2</sup>), maintaining a ratio of 4 g simulant/dm<sup>2</sup>. All the molds selected for this study were of the same size, so their surface area was calculated in cm<sup>2</sup> and the appropriate amount of Tenax® was used for the migration tests. The total contact surface calculated was 15.90 cm<sup>2</sup>, so the amount of Tenax® to be used in each test was 0.64 g.

According to Regulation (EU) No. 10/2011, the selected test conditions were 1 h at 175 °C, since it is estimated that the use of silicone molds for baking cupcakes is within that range, and would correspond to the worst conditions of use (longer time and temperature).

To carry out the migration test, simulant E (0.64 g) covered the entire bottom of the mold as a uniform layer. Given that the test conditions set were 1 h at 175 °C and that the compounds to be subsequently identified by SPME-GC-MS have volatile characteristics, the silicone molds were individually placed in hermetically sealed jars with silicone gaskets, as shown in [Fig. 2](#). A blank of Tenax® was simultaneously tested in order to eliminate the migration of volatile compounds from the sealing gaskets.

After being subjected to 175 °C for 1 h, the simulant continues to show the same initial physical characteristics, so it is easy to remove it from the mold and add it to a 20 mL vial to be subjected to the two sequential extractions with ethanol. For the extraction of Tenax®, the procedure described by [Aznar et al. \(2016\)](#) was followed. After decanting the Tenax® in a glass tube, 5 g of absolute ethanol (HPLC-grade) were added the set submitted for 1 h to sonication. It was then placed in a centrifuge for 10 min at 4000 rpm, the supernatant was collected and placed in a 20 mL vial. On the remaining Tenax®, 3 g of ethanol were added and the treatment was repeated for 1 h in an ultrasound bath and subsequent centrifugation. Finally, both supernatants from the extraction procedure were pooled. The ethanol extract obtained was analysed by solid phase microextraction coupled to gas chromatography (SPME-GC-MS). The samples were analysed by duplicate.

The migration tests that have been described were carried out directly with the silicone molds with and without post-cure treatment.

## 2.5. Analysis by SPME-GC-MS

For the analysis of the ethanol extracts resulting from the migration of silicone molds, SPME-GC-MS was selected as analytical technique, where the conditions of the SPME must be set: temperature, contact time and the type of SPME fiber to be used, since, depending on the polarity of the migrating compounds to be determined, there are different types that can be used. In this work, two types of fibers were selected DVB/CAR/PDMS fiber (divinylbenzene/carboxen/polydimethylsiloxane) with intermediate polarity and PDMS fiber (polydimethylsiloxane) with non-polar characteristics.

The use of SPME-GC-MS for the analysis of volatile compounds is limited by the % ethanol of the extract to be analysed. Previous studies carried out by [Asensio et al. \(2019\)](#) and [Asensio et al. \(2020\)](#), showed that diluting the ethanol extract with milliQ water to 20% allows the use of DVB/CAR/PDMS and PDMS SPME fibers with enough sensitivity, at ng/g level, required for the study. Therefore, for each ethanol extract obtained, 3 g were taken and 12 g of water were added, obtaining an extract to be analysed with 20% ethanol. The conditions for the analysis were as follows. SPME module (CTC Analytics Combi Pal auto sampler): SPME fiber (DVB/CAR/PDMS and PDMS), shaking at 500 rpm, incubation time 2 min, temperature 80 °C, extraction time 20 min and desorption time 2 min. Approximately 2 g of NaCl are added to all samples before their analysis. GC-MS chromatograph (Agilent 6809N with MS 5975B mass spectrometry detector): HP-5 capillary column (Agilent Technologies, Madrid, Spain), oven program: 50 °C for 5 min, ramp from 10 °C/min to 300 °C, hold 5 min. Acquisition in SCAN mode (m/z = 50–800). The identification of volatile compounds was carried out using the spectrum library present in the equipment's software (NIST Chemistry WebBook).

For the optimization of the type of fiber to be used (DVB/CAR/PDMS or PDMS) the extracts obtained from molds L and C were selected, and depending on the results obtained, one of them was selected for the complete study of the four silicone molds.

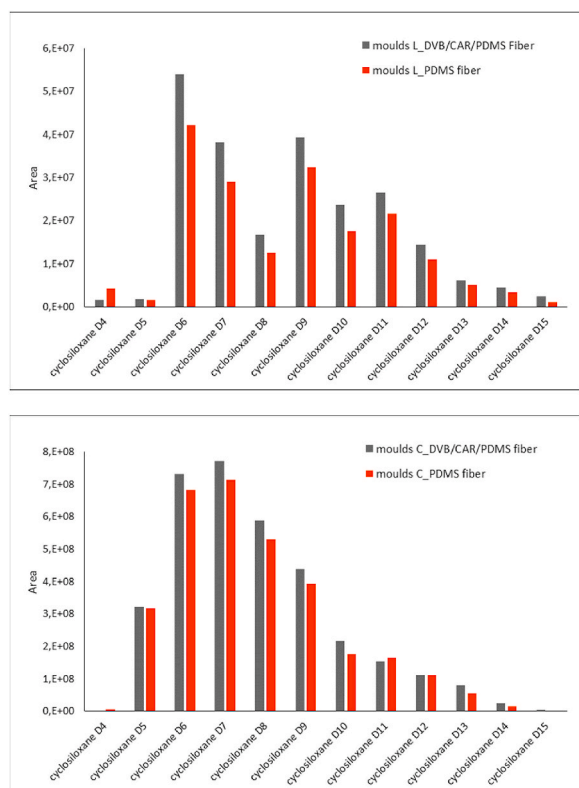
## 3. Results and discussion

### 3.1. Determination of VOC (%) compliance

To check whether silicone molds had received the correct heat treatment before being marketed, the loss of volatile compounds (VOCs) was evaluated to find if they exceeded the limit set by the [BfR standard \(2007\)](#), that is 0.5% (w/w). The results obtained after the evaluation of the four silicone molds studied are shown in [Table 1](#).

As can be seen in [Table 1](#), the experimental results obtained show that the highest quality silicone molds (L and S), made with platinum silicone, present losses less than 0.5% (w/w), meeting the requirements set by the BfR standard. While in the case of lower quality molds (C and CC), of which their specifications were not available, the weight losses (VOCs) were 1.2–2.0%, much higher than the established limit, 0.5%, showing that they had not been submitted to the required post-curing treatment.

According to these results, it could be said that the L and S silicone molds meet the requirements to be used at high temperature in contact with food when they are heated for the first time. While the silicone molds C and CC do not meet this requirement. Similar results were also observed in other studies carried out with silicone molds, by [Helling et al. \(2010\)](#), whose results showed that 18% of all silicone samples analysed contained more than 0.5% (w/w) of volatile substances, including siloxane oligomers. Studies carried out by [Meuwly et al. \(2005\)](#) showed a strong dependence of the amount of volatiles on the heating temperature and clearly indicated that the silicone molds are not as stable at high temperature as advertised by their manufacturers. More recently, studies carried out by [Liu et al. \(2021\)](#) showed initial values of total VOC concentration 2.53% higher than those recommended by the BfR Recommendations on food contact materials.



**Fig. 3.** a) and b). Identified cyclosiloxanes areas (D4 to D15) from migration extracts in molds L and C respectively for both types of SPME fiber studied. (use colour). (For interpretation of the references to colour in this figure legend, the reader is referred to the Web version of this article.)

For this reason, these lower quality molds (C and CC) should not be used in contact with food directly, that is, they should be heated successively without food in order to release VOCs until a constant weight loss of less than 0.5% (w/w). Since the latter is not feasible by the consumers who buy them, these molds should not be used directly. However, as there is no European legislation regarding the loss of VOCs,

only some recommendations, these molds meet the requirements to be used in food contact.

### 3.2. SPME fiber choice

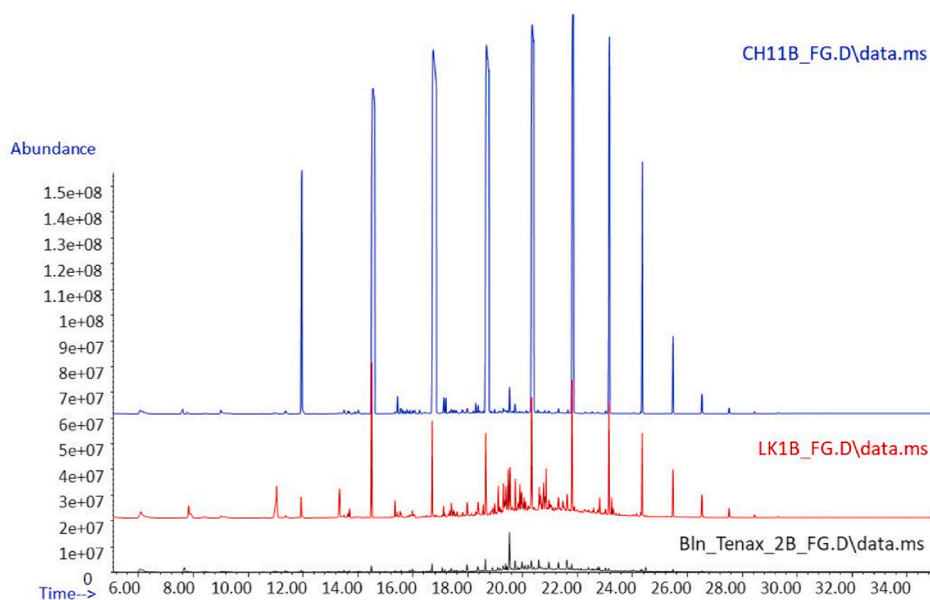
While the evaluation of the post-curing treatment applied to the silicone molds was being carried out, the optimization of the most suitable conditions for the analysis of siloxanes in the migration extracts was carried out. According to the work carried out by [Asensio et al. \(2019\)](#) the SPME conditions were studied: extraction temperature range 70–80 °C, extraction time range 15–30 min and type of fiber (DVB/CAR/PDMS and PDMS). In all cases, a stirring of 500 rpm, 2 min incubation time and desorption time of 2 min were used. The results did not improve with the addition of NaCl during the SPME extraction process. The results obtained showed that the best conditions were obtained with extraction temperature 80 °C, extraction time 20 min and DVB/CAR/PDMS fiber.

In addition, the chromatographic signal was higher when working with DVB/CAR/PDMS fiber compared to the use of PDMS fiber. To evaluate and select the best fiber for this analysis, the areas of identified cyclosiloxanes (D4 to D15) were plotted and are shown in [Fig. 3 a\) b\)](#).

As can be seen in [Fig. 3 a\) b\)](#), the best results, in both types of molds, correspond to the analyses carried out with the DVB/CAR/PDMS fiber. This performance is not surprising, as this fiber combines different polarities and is able to trap a wide range of molecular size compounds. Furthermore, a greater migration of cyclosiloxanes is observed in C mold compared to the L mold, but their quantification will be carried out later, together with the identification of other interesting compounds from the migration. According to the results obtained in the optimization step, the DVB/CAR/PDMS fiber was selected to carry out the analysis by SPME-GC-MS.

### 3.3. Results of migration studies

The extracts obtained from migration tests for the L and C molds were analysed, and the compounds found were identified as siloxanes, according to the spectral library of the GC-MS (NIST Chemistry WebBook) with more than 90% similarity versus the MS spectra from the library. Kovats indices were determined to a correct tentative identification of the compounds. The chromatograms obtained for each type of



**Fig. 4.** SPME-GC-MS chromatograms of blank of Tenax (black), mold L (red) and mold C (blue). (use colour). (For interpretation of the references to colour in this figure legend, the reader is referred to the Web version of this article.)

**Table 2**  
Identification (●) of volatile migrants after analysis of ethanol extracts by SPME-GC-MS (with and without post-cure treatment).

tr (min)	CAS No.	Compounds	Molds without post-cure				Molds with post-cure				Restrictions	KI <sup>a</sup>
			L	S	C	CC	L	S	C	CC		
8.99	556-67-2	octamethylcyclotetrasiloxane(D4)	●	●	●	●	●	●	●	●	b	955
11.93	541-02-6	decamethylcyclopentasiloxane(D5)	●	●	●	●	●	●	●	●	b	1137
12.83	91-20-3	naphthalene					●	●	●	●	NOAEL 100 <sup>2</sup>	1191
14.49	540-97-6	dodecamethylcyclohexasiloxane(D6)	●	●	●	●	●	●	●	●	b	1306
15.18	2409-55-4	2-tert-butyl-4-methylphenol					●	●	●	●	NOAEL 2400 <sup>2</sup>	1350
15.71	92-52-4	1,1-biphenyl					●	●	●	●	NOAEL 50 <sup>2</sup>	1388
15.79	1120-36-1	1-tetradecene			●						NOAEL 100 <sup>2</sup>	1394
15.89	629-59-4	tetradecane	●	●		●					Cramer class I	1400
16.42	128-39-2	2,6-di-tert-butylphenol	●				●				NOAEL 100 <sup>2</sup>	1442
16.70	107-50-6	tetradecamethylcycloheptasiloxane(D7)	●	●	●	●	●	●	●	●	b	1463
16.78	719-22-2	2,6-di-tert-butylquinone	●								Cramer class II	1469
17.20	629-62-9	pentadecane	●	●	●	●					Cramer class I	1500
17.30	128-37-0	2,6-ditert-butyl-4-methylphenol(BHT)				●				●	SML 3 mg/kg	1510
17.61	541-01-5	hexadecamethylheptasiloxane(L7)	●								b	1536
17.87	2801-87-8	4-methylpentadecane		●							Cramer class I	1557
18.29	629-73-2	1-hexadecene			●	●					NOAEL 1000 <sup>2</sup>	1592
18.41	544-76-3	hexadecane	●	●		●					Cramer class I	1600
18.56	124-25-4	tetradecanal				●					Cramer class I	1615
18.64	556-68-3	hexadecamethylcyclooctasiloxane(D8)	●	●	●	●		●	●		b	1622
18.92	119-61-9	benzophenone				●					SML 0.6 mg/kg	1646
18.94	3892-00-0	2,6,10-trimethylpentane		●							Cramer class I	1648
19.11	629-82-3	1-octoxyoctane	●								Cramer class I	1663
19.12	1560-92-5	2-methylhexadecane		●							Cramer class I	1664
19.46	2156-97-0	dodecyl acrylate	●								SML 0.05 mg/kg	1694
19.57	629-78-7	heptadecane		●		●					Cramer class I	1700
19.89	24157-81-1	2,6-diisopropyl-naphthalene	●	●	●	●					Cramer class III	1733
20.22	1560-89-0	2-methylheptadecane		●							Cramer class I	1763
20.32	556-71-8	octadecamethylcyclononasiloxane(D9)	●	●	●	●				●	b	1772
20.64	593-45-3	octadecane	●	●		●					Cramer class I	1800
20.70	638-36-8	2,6,10,14-tetramethylhexadecane		●							Cramer class I	1808
20.74	118-60-5	2-ethylhexyl salicylate	●								Cramer class I	1812
20.80	112-88-9	1-octadecene		●							Cramer class I	1818
20.84	110-27-0	isopropyl myristate	●								Cramer class I	1822
21.64	629-92-5	nonadecane		●		●					Cramer class I	1900
21.80	18772-36-6	eicosamethylcyclododecasiloxane(D10)	●	●	●	●					b	1919
21.88	112-39-0	hexadecanoic acid, methyl ester		●							Cramer class I	1927
22.31	57-10-3	hexadecanoic acid			●						SML <60 mg/kg	1971
22.58	628-97-7	ethyl hexadecanoate								●	Cramer class I	1999
22.59	112-95-8	eicosane		●		●				●	NOAEL 1000 <sup>2</sup>	2000
22.80	142-91-6	isopropyl palmitate	●								Cramer class I	2023
23.14	18766-38-6	docosamethylcycloundecasiloxane(D11)	●	●	●	●					b	2060
23.77	2490-23-5	methyl 14-methylheptadecanoate				●					Cramer class I	2139
24.19	629-97-0	docosane								●	Cramer class I	2200
24.36	18919-94-3	tetracosamethylcyclododecasiloxane(D12)	●	●	●	●					b	2216
25.47	23732-94-7	hexacosamethylcyclotridecasiloxane(D13)	●	●	●	●					b	2329
26.53	149050-40-8	octacosamethylcyclotetradecasiloxane(D14)	●	●	●	●					b	2462
27.52	23523-14-0	triacontamethylcyclopentadecasiloxane(D15)	●	●	●	●					b	2483

cExpressed as mg/kg bw-d.

<sup>a</sup> Kovats retention Index.

<sup>b</sup> Total <10 mg/dm<sup>2</sup> Specific Limit Migration (SLM) by Regulation (UE) No. 10/2011.

**Table 3**  
Correlation coefficients, working range, and LOD and LOQ for the available standards.

Compounds	Correlation coefficient	Working range (ng/g)	LOD (ng/g)	LOQ (ng/g)
octamethylcyclotetrasiloxane	0.9988	0.5–8	0.10	0.43
decamethylcyclopentasiloxane	0.9994	0.5–18	0.14	0.46
dodecamethylcyclohexasiloxane	0.9940	0.5–17	0.14	0.45
butylated hydroxytoluene	0.9980	0.6–5.0	0.17	0.58
	0.9987	8.0–130		
hexadecanoic acid	0.9988	0.5–5.0	0.17	0.56
hexadecanoic acid, methyl ester	0.9955	0.6–14	0.18	0.61
2,6-diisopropyl-naphthalene	0.9919	3.0–100	0.09	3.10

molds for cupcakes with DVB/CAR/PDMS fiber are compared in Fig. 4.

Fig. 4 shows that mold C (lower quality) provided the highest number of volatile migrants compared to mold L (higher quality). These

data agree with the results obtained from the analysis of the % of VOCs released, where the C mold losses were more than 0.5% (w/w).

Regulation (EU) No 10/2011 specifies the specific migration limits (SML), “maximum allowed amount of a given substance released from a material or object in food or food simulants”, which must be met by the substances that appear in Annex I. In addition, and according to Royal Decree 847/2011, their components must not be transferred to food products in quantities that exceed 10 mg/dm<sup>2</sup> and for substances that do not have a specific migration limit, or any other restriction, a generic global migration limit of 60 mg/kg will be applied to them. For compounds that do not present a migration limit in the legislation, it will be necessary to check if they present NOAEL values (No Observed Adverse Effect Level), which is a toxicity index that is determined in the “toxicological evaluation” process, and from it the rest of the toxicity parameters. If this is not the case, the toxicity level can be estimated by a theoretical approach based on chemical structure, according to the Cramer rules and the Threshold of Toxicological Concern (TTC) using the Toxtree v3.1.0.1851 application. It establishes three TTC levels, I, II

**Table 4a**

Quantification (D4, D5 and D6) and semi-quantification of silicone oligomers, expressed as  $\mu\text{g}/\text{dm}^2$ , identified in the silicone molds studied with and without post-cure treatment.

Compounds	Concentration ( $\mu\text{g}/\text{dm}^2$ ) molds without post-cure treatment			
	L	S	C	CC
octamethylcyclotetrasiloxane(D4)	2.3 ± 1.1	9.4 ± 0.9	10.3 ± 1.5	2.1 ± 0.1
decamethylcyclopentasiloxane(D5)	23.7 ± 15.6	31.3 ± 4.9	611.7 ± 75.7	136.9 ± 8.4
dodecamethylcyclohexasiloxane(D6)	354.4 ± 91.6	69.0 ± 8.8	(27.3 ± 0.4) × 10 <sup>2</sup>	(18.8 ± 0.9) × 10 <sup>2</sup>
tetradecamethylcycloheptasiloxane (D7)*	187.6 ± 33.6	45.1 ± 13.8	(36.0 ± 1.9) × 10 <sup>2</sup>	(28.2 ± 1.0) × 10 <sup>2</sup>
hexadecamethylheptasiloxane(L7)*	11.6 ± 1.9	–	–	–
hexadecamethylcyclooctasiloxane(D8)*	69.6 ± 40.1	160.2 ± 27.1	(31.6 ± 1.8) × 10 <sup>2</sup>	(26.8 ± 0.3) × 10 <sup>2</sup>
octadecamethylcyclononasiloxane(D9)*	179.3 ± 61.8	214.3 ± 12.4	(25.1 ± 0.7) × 10 <sup>2</sup>	(21.8 ± 1.0) × 10 <sup>2</sup>
eicosamethylcyclodecasiloxane(D10)*	183.0 ± 53.9	112.5 ± 23.3	(17.3 ± 0.3) × 10 <sup>2</sup>	(14.4 ± 0.8) × 10 <sup>2</sup>
docosamethylcycloundecasiloxane (D11)*	137.9 ± 45.0	67.2 ± 15.8	(10.1 ± 0.3) × 10 <sup>2</sup>	895.6 ± 112.4
tetracosamethylcyclododecasiloxane (D12)*	105.7 ± 31.7	52.4 ± 16.9	492.4 ± 0.1	460.3 ± 100.2
hexacosamethylcyclotridecasiloxane (D13)*	65.5 ± 18.8	29.3 ± 9.7	79.9 ± 7.3	140.6 ± 40.2
octacosamethylcyclotetradecasiloxane (D14)*	30.3 ± 12.1	11.7 ± 2.3	34.4 ± 1.9	35.3 ± 3.5
triacontamethylcyclopentadecasiloxane (D15)*	11.6 ± 4.0	4.6 ± 0.5	8.1 ± 0.6	6.7 ± 2.9
Total ( $\text{mg}/\text{dm}^2$ ) silicone oligomers	1.4	0.8	16.0	12.7
Compounds	Concentration ( $\mu\text{g}/\text{dm}^2$ ) molds with post-cure treatment			
	L	S	C	CC
octamethylcyclotetrasiloxane(D4)	6.4 ± 0.9	25.9 ± 6.0	2.0 ± 0.5	5.6 ± 0.5
decamethylcyclopentasiloxane(D5)	8.3 ± 1.0	30.2 ± 4.9	3.9 ± 0.9	6.2 ± 0.1
dodecamethylcyclohexasiloxane(D6)	4.9 ± 0.2	10.7 ± 0.1	3.6 ± 0.3	7.0 ± 0.1
tetradecamethylcycloheptasiloxane (D7)*	4.1 ± 0.3	4.1 ± 0.1	4.1 ± 1.0	9.8 ± 1.0
hexadecamethylheptasiloxane(L7)*	–	–	–	–
hexadecamethylcyclooctasiloxane(D8)*	–	–	0.1 ± 0.0	4.8 ± 2.9
octadecamethylcyclononasiloxane(D9)*	–	–	–	2.5 ± 0.3
eicosamethylcyclodecasiloxane(D10)*	–	–	–	0.4 ± 0.0
Total ( $\text{mg}/\text{dm}^2$ ) silicone oligomers	0.02	0.1	0.01	0.04

\* semi-quantification silicone oligomers with standard of siloxane (D5).

and III, from lowest to highest toxicity, with a limit of 30; 9 and 1.5  $\mu\text{g}/\text{kg}$  bw-d, respectively.

Table 2 shows the results obtained after analysing the ethanol extracts by SPME-GC-MS. In addition to the migration of cyclosiloxanes, it is important to consider other volatile compounds that migrate and should be also quantified and controlled.

In the case of molds subjected to post-cure treatment, two compounds, naphthalene and 1,1-biphenyl, were found in all samples (L, S, C and CC molds). These compounds have restrictions, with NOAEL values of 100  $\text{mg}/\text{kg}$  bw-d and 50  $\text{mg}/\text{kg}$  bw-d, respectively. The presence of 1,1-biphenyl could be attributed to decomposition of silicone elastomer.

Furthermore, in the case of CC molds, the migration of 2-tert-butyl-4-methylphenol and eicosane (used as an emollient and surfactant) has been identified, which have a NOAEL of 2400  $\text{mg}/\text{kg}$  bw-d and 1000  $\text{mg}/\text{kg}$  bw-d, respectively. Cyclopentadecanol, classified as class II according to Cramer, must be lower than 9  $\mu\text{g}/\text{kg}$  bw-d and ethyl hexadecanoate and docosane, classified as class I according to Cramer must be lower than 30  $\mu\text{g}/\text{kg}$  bw-d.

In addition, 2,6-ditert-butyl-4-methylphenol (BHT), a common antioxidant in plastics and food with a SML of 3  $\text{mg}/\text{kg}$ , was identified in CC molds with and without post-cure treatment. Feng et al. (2016) analysed silicone rubber teats for babies using SPME-GC-MS, and also identified the presence of naphthalene, (BHT) and dodecane. The presence of dodecane (alkane) could be due to the use of machine oil (lubricant) during the manufacture of the molds. Likewise, Lund and Petersen (2002) also identified BHT in soothers and teats.

In the case of molds not subjected to post-cure treatment, a series of alkanes (from C14 to C20) were identified mainly in the L, S and CC molds. In the four types of molds 2,6-DiPNs isomers classified as class III by Cramer were identified. In molds C and CC, the hexadecanoic acid was also identified, both without SML according to Regulation (EU) No 10/2011.

Benzophenone with an SML of 0.6  $\text{mg}/\text{kg}$  was identified in the CC molds. And finally, 2,6-ditert-butylcyclohexa-2,5-diene-1,4-dione and heptanoyl heptanoate, classified as class II and class III, respectively, and dodecyl acrylate with an SML of 0.05  $\text{mg}/\text{kg}$  were identified in the L molds.

Low molecular weight cyclosiloxanes, mainly the octamethylcyclotetrasiloxane, decamethylcyclopentasiloxane and dodecamethylcyclohexasiloxane (D4, D5 and D6, respectively), are the most important raw materials for preparing silicone polymers (Hori and Kannan, 2008; Tran and Kannan, 2015). Therefore, silicone products could inevitably contain such siloxane monomers that react incompletely during the production process, including cyclic and linear siloxanes (Liu et al., 2020).

As shown in Table 2, thirteen cyclic siloxanes (from D4 to D15) and one linear siloxane (L7) were identified in the migration extracts of the silicone molds. It can be observed that the number of cyclosiloxanes that migrate, after subjecting the molds to post-cure treatment, is greater in the lower quality molds, migrating cyclosiloxanes D4 to D8 in molds C and up to D9 in molds CC. This performance agrees with what was observed in the optimization step of the SPME-GC-MS methodology. In the molds L and S, only cyclosiloxanes D4 to D7 migrate. In the molds without post-cure treatment, cyclosiloxanes D4 to D15 were identified, and in the particular case of the molds L, a linear siloxane (L7) was also identified. Differences are seen in the concentration of cyclosiloxanes between the different molds, as will be discussed later.

It is important to note that in the particular case of the molds CC with post-cure treatment and in the case of all molds without post-cure treatment, more chromatographic peaks were found that could not be identified using the spectral library of the GC MS equipment (NIST Chemistry WebBook) but they could be classified as siloxanes, as residual compounds from the polymerization process or the result of chemical reactions during processing. It would be very interesting to continue studying them and identify and quantify these siloxanes.

For quantify the siloxanes oligomers identified in the ethanol extracts after the migration tests octamethylcyclotetrasiloxane (D4), decamethylcyclopentasiloxane(D5) and dodecamethylcyclohexasiloxane (D6) standards were used. A calibration line was prepared and analysed by SPME-GC-MS under the same conditions as the samples. A stock solution was prepared, in absolute ethanol, with a concentration of 981.24  $\mu\text{g}/\text{g}$ ; 998.38  $\mu\text{g}/\text{g}$  and 831.05  $\mu\text{g}/\text{g}$ , respectively. The five different points of the calibration curve were prepared with a 20% ethanol (the same as in the samples) and a concentration between 1 and 18  $\text{ng}/\text{g}$ , all of them controlled by weighing. From the calibration line obtained the concentrations expressed in  $\text{mg}/\text{dm}^2$  were calculated and compared to the specific migration limit established by the legislation. For the semi-

**Table 4b**

Quantification and semi-quantification of volatile migrants, expressed as mg/kg Tenax®, identified in the silicone molds.

Compounds	Concentration (mg/kg Tenax) molds without post-cure treatment				Restrictions
	L	S	C	CC	
octamethylcyclotetrasiloxane(D4)	0.6 ± 0.02	2.3 ± 0.1	2.6 ± 0.3	0.5 ± 0.3	
decamethylcyclopentasiloxane(D5)	5.9 ± 0.4	7.8 ± 1.2	152.0 ± 18.8	34.0 ± 2.1	
dodecamethylcyclohexasiloxane(D6)	87.8 ± 9.3	17.1 ± 2.2	677.6 ± 10.3	466.2 ± 21.5	
2,6-di-tert-butylphenol <sup>2</sup>	0.2 ± 0.03	–	–	–	<100 mg/kg bw-d
tetradecamethylcycloheptasiloxane(D7) <sup>1</sup>	46.5 ± 8.3	11.2 ± 3.4	895.0 ± 47.5	698.8 ± 25.9	
2,6-di-tert-butylquinone <sup>2</sup>	0.3 ± 0.1	–	–	–	9 µg/kg bw-d
butylated hydroxytoluene(BHT)	–	–	–	29.1 ± 2.2	<3 mg/kg
hexadecamethylheptasiloxane(L7) <sup>1</sup>	2.9 ± 0.5	–	–	–	
hexadecamethylcyclooctasiloxane(D8) <sup>1</sup>	17.2 ± 9.9	39.8 ± 6.7	784.5 ± 44.8	664.3 ± 7.4	
2,6-diisopropyl-naphthalene	47.8 ± 8.1	113.7 ± 4.3	–	10.4 ± 0.1	1,5 µg/kg bw-d
octadecamethylcyclononasiloxane(D9) <sup>1</sup>	44.4 ± 15.3	53.2 ± 3.1	622.8 ± 16.4	541.1 ± 25.2	
eicosamethylcyclotetradecasiloxane(D14) <sup>1</sup>	45.3 ± 13.4	28.0 ± 5.8	429.8 ± 6.2	356.9 ± 18.9	
hexadecanoic acid, methyl ester	7.1 ± 1.6	13.2 ± 2.4	–	–	30 µg/kg bw-d
hexadecanoic acid	–	–	4.3 ± 0.01	–	<60 mg/kg
isopropyl palmitate <sup>3</sup>	10.6 ± 1.8	–	–	–	30 µg/kg bw-d
docosamethylcyclododecasiloxane(D11) <sup>1</sup>	34.1 ± 11.2	16.7 ± 3.9	250.4 ± 7.1	222.3 ± 27.9	
tetracosamethylcyclododecasiloxane(D12) <sup>1</sup>	26.1 ± 7.9	13.0 ± 4.2	122.3 ± 13.1	114.2 ± 24.9	
hexacosamethylcyclotridecasiloxane(D13) <sup>1</sup>	16.2 ± 4.7	7.3 ± 2.4	19.8 ± 6.7	34.9 ± 10.0	
octacosamethylcyclotetradecasiloxane(D14) <sup>1</sup>	7.5 ± 3.0	2.9 ± 0.6	8.6 ± 0.5	8.8 ± 3.0	
triacontamethylcyclopentadecasiloxane(D15) <sup>1</sup>	2.9 ± 1.0	1.1 ± 0.1	2.0 ± 0.1	1.7 ± 0.8	
Compounds	Concentration (mg/kg Tenax) molds with post-cure treatment				Restrictions
	L	S	C	CC	
octamethylcyclotetrasiloxane(D4)	1.6 ± 0.3	6.4 ± 1.5	0.5 ± 0.02	1.4 ± 0.1	
decamethylcyclopentasiloxane(D5)	2.1 ± 0.2	7.5 ± 1.2	1.0 ± 0.1	1.5 ± 0.03	
2-tert-butyl-4-methylphenol <sup>2</sup>	–	–	–	0.1 ± 0.01	<2400 mg/kg-d
dodecamethylcyclohexasiloxane(D6)	1.2 ± 0.04	2.6 ± 0.02	0.9 ± 0.05	1.7 ± 0.03	
2,6-di-tert-butylphenol <sup>2</sup>	0.1 ± 0.002	–	–	–	<100 mg/kg-d
tetradecamethylcycloheptasiloxane(D7) <sup>1</sup>	1.0 ± 0.1	1.0 ± 0.004	1.0 ± 0.3	2.4 ± 0.3	
hexadecamethylheptasiloxane(L7) <sup>1</sup>	–	–	–	–	
hexadecamethylcyclooctasiloxane(D8) <sup>1</sup>	–	–	0.02 ± 0.005	1.2 ± 0.7	
octadecamethylcyclononasiloxane(D9) <sup>1</sup>	–	–	–	0.6 ± 0.03	
eicosamethylcyclododecasiloxane(D10) <sup>1</sup>	–	–	–	0.1 ± 0.005	

<sup>1</sup> semi-quantified as decamethylcyclopentasiloxane (D5).<sup>2</sup> semi-quantified as butylated hydroxytoluene and.<sup>3</sup> semi-quantified as hexadecanoic acid.

quantification of the other siloxanes identified, it was decided to use the calibration line obtained for decamethylcyclopentasiloxane.

For the quantification and semi-quantification of other compounds identified together with the siloxanes, the corresponding calibration plots were prepared for butylated hydroxytoluene (BHT), hexadecanoic acid, hexadecanoic acid, methyl ester and 2,6-diisopropyl-naphthalene. Correlation coefficients, working range, and LOD and LOQ for the cyclosiloxane D5 and available standards are shown in Table 3.

The results (semi-quantification with siloxane oligomer D5) obtained are shown in Tables 4a and 4b, expressed in µg/dm<sup>2</sup> and in mg/kg Tenax®. The analyses were carried out by triplicate and the value expressed is the average value.

From the results shown in Table 4a, it can be seen that without post-cure treatment, samples C and CC exceed the total migration limit of 10 mg/dm<sup>2</sup>, so they do not comply with the Regulations relating to materials in contact with food. These results agree with those obtained from the loss of volatile compounds (VOC), where these two types of molds exceeded the recommended 0.5% loss, and therefore their direct use as material in contact with food is not recommended. In the case of molds L, the cyclosiloxane with the highest migration is D6, in molds S it is D9 and in D7 in molds C and CC. The results of the migration from the molds with post-cure treatment showed that none of the four molds exceeds the overall migration limit of 10 mg/dm<sup>2</sup>, although in the case of L and S molds only oligomers of silicones D4 to D7 were observed, while in molds C and CC were identified up to D8 and D10, respectively.

Liu et al. (2020), carried out migration studies in silicone molds using Tenax® as a food simulant and determined concentrations of D4, D5, and D6 of 0.9; 2.2 and 2.7 mg/kg, respectively before subjecting to cyclical heating in oven and microwave.

According to the results shown in Table 4b the migration in Tenax® before subjecting the molds to post-cure treatment shows values between 0.5 mg/kg Tenax® (D4 in CC mold) and 677.6 mg/kg Tenax® (D6 in C mold), above the initial concentrations of the study by Liu et al. (2020). However, the migration observed after the post-cure treatment, for these three (3) cyclosiloxanes shows values between 0.5 mg/kg Tenax® (D4 in C mold) and 2.1 mg/kg Tenax® (D5 in L mold) within the range of concentrations of the study by Liu et al. (2020), except for the particular case of the S molds that shows much higher migration values of up to 6.4; 7.5 and 2.6 mg/kg Tenax® for D4, D5 and D6, respectively.

Feng et al. (2019) carried out a series of studies to determine by P&T-GC-MS the concentration of volatile cyclosiloxanes (D4, D5 and D6) in silicone samples for food contact. In this study they found concentrations of 3.4; 69.8 and 23.1 mg/kg in silicone teats, and 42.8; 57.0 and 22.4 mg/kg in silicone bakeware. These values give an idea of the migration that can take place when these silicone materials come into contact with food. The present work shows higher concentrations in mg/kg Tenax® for these three cyclosiloxanes (D4, D5 and D6), especially when the molds have not been subjected to post-cure treatment.

Another study carried out by Fromme et al. (2019) that includes the study of the migration of cyclosiloxanes in food directly in cake samples cooked in silicone bakeware, shows mean concentrations of 0.1; 0.4; 1.2; 2.6 and 3.2 mg/kg of D4, D5, D6, D7 and D8 respectively. These values are similar to those obtained in this work with Tenax® as food simulant, only with molds with post-cure treatment. The migration observed with the molds without post-cure treatment was much higher, as already mentioned.

Regarding the rest of the quantified compounds, in the molds without post-cure treatment, two compounds that have SML (Regulation

(EU) No 10/2011) were quantified, and among them hexadecanoic acid (molds C) does not exceed the limit, while in the case of the CC molds, butylated hydroxytoluene (BHT) concentrations of 29.1 mg/kg Tenax® were well above the limit set at 3 mg/kg. For 2,6-di-tert-butylphenol (molds L), concentrations lower than the NOAEL value (100 mg/kg bw-d) were found. While 2,6-di-tert-butylquinone (molds L), 2,6-diisopropyl naphthalene (molds L, S and CC), hexadecanoic acid, methyl ester (molds L and S) and isopropyl palmitate (molds L) exceed the recommended limits based on the corresponding Cramer class.

In the molds with post-cure treatment, 2-tert-butyl-4-methylphenol and 2,6-di-tert-butylphenol were quantified, in CC and L molds, respectively. In both cases, the quantified values were much lower than the NOAEL values.

#### 4. Conclusions

In this work the safety of several selected silicone molds was evaluated to confirm if they were appropriate as food contact materials. The results obtained indicate that in the case of molds selected from manufacturers that certify the quality of the product, the treatment received before their commercialization was adequate, showing a loss of volatile compounds (VOCs) that does not exceed 0.5% (w/w), as recommended for silicone products or utensils. However, molds from lower quality manufacturers showed a loss of VOCs that exceeds the recommended value 0.5% (w/w) established by BfR.

The migration of twelve cyclosiloxanes (from D4 to D15) and one linear siloxane (L7) have been identified and quantified in this study. In the case of the molds with post-cure treatment, none of them presented a migration higher than the limit of 10 mg/dm<sup>2</sup> established by the legislation. However, in the case of molds C and CC without post-cure treatment, they exceed the migration limit with values of 15.97 and 12.67 mg/dm<sup>2</sup>. Therefore, they should not be used in contact with food at high temperature.

In addition to cyclosiloxanes, other compounds in the extracts resulting from migration were identified and quantified, such as naphthalene, 1,1-biphenyl, 2-tert-butyl-4-methylphenol, 2,6-di-tert-butyl-4-methylphenol, dodecyl acrylate, hexadecanoic acid, and eicosane, which are used as emollients, surfactants, lubricants and antioxidants. Some of which have specific migration limits (mg/kg) or NOAEL values (mg/kg bw-d).

#### CRedit authorship contribution statement

**Esther Asensio:** Conceptualization, Validation, Formal analysis, Investigation, Data curation, Writing – original draft, Writing – review & editing, Supervision. **Joaquín Uranga:** Methodology, Validation, Investigation, Data curation. **Cristina Nerín:** Conceptualization, Resources, Writing – review & editing, Supervision, Project administration, Funding acquisition.

#### Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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