



Safety assessment of silicone molds for food use: A comprehensive analysis of migration patterns and volatile compound release in European markets

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ABSTRACT

Silicones can contain oligomers known as siloxanes, which are either by-products of the polymerization process or arise from chemical reactions during processing. They may also have both intentionally and non-intentionally added substances, making it crucial to verify that silicone molds are safe and appropriate for food use. In this study 44 silicone molds available in the market from different European countries were studied. Triple sequential migration assays at 100 °C for 8 h each using food simulants (3 % acetic acid, 20 % ethanol, and 50 % ethanol) were conducted. Some samples were also tested 4 h at 100 °C. Global migration assessments were only conducted on turbid samples, while qualitative and quantitative analyses of volatile compounds were performed using solid phase microextraction-gas chromatography-mass spectrometry (SPME-GC-MS) in total immersion mode. During the screening analysis of samples of 50 % ethanol at 100 °C for 8 h a total of 112 different volatile compounds were tentatively identified by MS spectra and quantitatively estimated (LODs = 0.00005–0.014 mg/kg). However, there was no observable migration in the case of 3 % acetic acid and 20 % ethanol. All samples comply with the legislation (Royal Decree 847/2011) in the case of siloxanes. Some samples exceeded specific migration limits for volatile compounds other than siloxanes after third migration in 50 % EtOH at 100 °C for 8 h.

1. Introduction

The popularity of silicone materials in the kitchen is due to their friendly use, flexibility, and availability in various shapes and colours (Liu et al., 2021). Consumers choose silicone for numerous culinary preparations involving the oven or the freezer (Han et al., 2022). Silicone materials have experienced high demand due to their non-stick capabilities and the convenience they offer for cleaning, as they can be washed directly in the dishwasher (Feng et al., 2023).

There is not a harmonized legislation in Europe for silicones, but national legislations apply in addition to the framework Regulation (EC) No 1935/2004 (European Commission Regulation, 2004). In Spain, the Royal Decree 847/2011 (The Ministry of Health, 2011) sets out a list of monomers, additives and other starting substances permissible in the production of adhesives, elastomers, and natural and synthetic rubbers; ion exchange resins; silicones and varnishes; coatings; and plastic materials in contact with food not covered by Annex I of Regulation (EU) No 10/2011 and its amendments (European Union Commission

Regulation EU, 2011).

Silicones can contain oligomers, called siloxanes, which are residual compounds from the polymerization process or the result of chemical reactions during processing (Elskens et al., 2012; Feng et al., 2019). These siloxanes may not be totally inert when in contact with fatty foods (Helling et al., 2010, 2009, 2012).

Silicone materials can contain intentionally added substances (IAS) (Helling, Seifried, Fritzsche, & Simat, 2012; Asensio, Uranga, & Nerín, 2022; Krüger et al., 2021; Shit & Shah, 2013; Cederberg and Jensen, 2017), typically employed to enhance the physical-chemical properties of materials, for example, their plasticity or moldability (García Ibarra et al., 2019, 2018). But they can also contain non-intentionally added substances (NIAS) that originate from impurities in the raw material itself, degradation compounds that occur during manufacturing process or substances resulting from the interaction with reagents (Galbiati et al., 2022; Nerín et al., 2013; Portesi et al., 2019; Song et al., 2019; Vera et al., 2018). Unfortunately, silicone materials used for cooking can transfer IAS and NIAS to food (Liu et al., 2021; Asensio et al., 2022).

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Among them phthalates, primarily used as plasticizers in packaging and known endocrine disruptors (Ji et al., 2013) can be found.

As happens with any other food contact material, it is imperative to ensure that the available silicone molds are harmless and suitable for food use. Therefore, in accordance with previously mentioned European (European Commission Regulation, 2004) and national regulations, it is necessary to check the likely release of harmful substances from silicone molds to the food in contact with them (Wrona & Nerín, 2020, 2019). The specific migration limit is assigned to many individual substances or chemical families. Although silicones as food contact materials are present in many devices, their main use is in bakery molds, at both industrial level and in domestic uses and almost all of them involve high temperature applications (100–200 °C), what increases the release of compounds and thus the risk for consumers.

Additionally, materials and objects must not exceed the maximum migration limit of either 10 mg of constituents released per dm² of surface area or 60 mg/kg of those compounds without specific migration limit in Royal Decree 847/2011 (The Ministry of Health, 2011).

The present work was part of a European project by the International Consumer Research and Testing Limited (COAC) to evaluate the safety in use of silicone molds in the European market. As the current laws only regulate the presence of monomers, additives, and other initial ingredients (The Ministry of Health, 2011), the presence of NIAS could pose a risk to food safety. Therefore, the main objective of this work was to examine the potential substances possibly relevant for migration to food simulants in contact with silicone molds, when subjected to high temperature (100 °C).

2. Material and methods

2.1. Samples

For the purpose of the project, COAC provided forty-four silicone

mould samples with varied shapes, sizes, colours and brands for a comprehensive analysis of all types of silicone moulds available in the market. The samples were purchased at the vendors and they were received in cardboard boxes, packaged as they were sold in the markets. The moulds were categorized into nine groups with five samples in groups 1–8 and four samples in group 9. The samples were labelled from M1 to M44. Table 1 shows the list of analyzed samples with their origin and the denomination.

2.2. Reagents

Octamethylcyclotetrasiloxane (D4) (98 %, CAS 556-67-2), decamethyl-cyclopentasiloxane (D5) (97 %, CAS 541-02-6), dodecamethylcyclohexasiloxane (D6) (95 %, CAS 540-97-6), undecanal (CAS 112-44-7), trans-2-decenal (CAS 3913-81-3), hexadecanoic acid (CAS 57-10-3), octadecanoic acid (CAS 57-11-4), 2,6-diisopropyl-naphthalene (99 %, CAS 24157-81-1), 2(3H)-furanone, dihydro-5-tetradecyl- (97 %, CAS 502-26-1), oleamide (CAS 301-02-0), diethyl phthalate (99.5 %, CAS 84-66-2), diisobutyl phthalate (99 %, CAS 84-69-5), dibutyl phthalate (99 %, 84-74-2), benzyl butyl phthalate (CAS 85-68-7) and bis (2-ethylhexyl) phthalate (CAS 117-81-7) used as analytical standards for quantification were from Sigma-Aldrich (Madrid, Spain). A mixture of n-alkanes (C7-C40) in hexane at a concentration of approximately 1000 µg/g was also obtained from Sigma-Aldrich (Madrid, Spain). Ethanol (EtOH) of HPLC-grade and acetic acid were used from Scharlab (Madrid, Spain). Ultrapure water was obtained from a Wasserlab Ultramatic GR system located in Barbatáin, Spain. The analytical standards stock solutions were gravimetrically prepared at concentrations around 1000 µg/g in absolute ethanol. Corresponding calibration curve dilutions were prepared in 20 % EtOH with ultrapure water from standardized stock solutions. These solutions were injected into the SPME-GC-MS equipment in total immersion mode of the SPME fiber within 24 h of their preparation. The list of standards used for quantification of

Table 1
List of analyzed silicone molds samples.

No	Country	Figure	No	Country	Figure	No	Country	Figure	No	Country	Figure
M1	All		M14	All		M27	Austria/Denmark		M40	France	
M2	All		M15	All		M28	Austria		M41	France	
M3	All		M16	Italy		M29	Austria		M42	France	
M4	All		M17	All		M30	Austria		M43	France	
M5	All		M18	All		M31	Portugal		M44	France	
M6	All		M19	All		M32	Portugal				
M7	All		M20	All		M33	Denmark/Sweden				
M8	All		M21	Italy		M34	Denmark				
M9	All		M22	Italy		M35	Sweden				
M10	All		M23	Italy		M36	Sweden				
M11	All		M24	Spain		M37	Belgium				
M12	All		M25	Spain		M38	Belgium				
M13	All		M26	Spain		M39	Belgium				

*All means that molds are available in all countries of European Union.

each detected compound and analytical parameters such as limits of detection and quantification are presented in [supplementary materials](#).

2.3. Migration test conditions

Royal Decree 847/2011 ([The Ministry of Health, 2011](#)) specifies that migration tests will be conducted under the most extreme conditions to represent the worst scenario of real use to ensure compliance with maximum allowable limits. According to the Guidelines published by Joint Research Centre (JRC) from European Commission ([Beldi et al., 2023](#)) for kitchenware utensils and specifically for silicone molds, the test should be carried out either 2 h at 175 °C, or 4 h at 100 °C under reflux or 8 h at 100 °C under reflux, depending on the intended use. However, it is noted that for cases using simulant A, B, C, or D1, the test can be replaced by treatment at 100 °C or reflux temperature, lasting four times longer than the initially selected time.

In this optimization study, D1 simulant was used, and three silicone molds (samples M3, M19, and M20) were initially chosen. Migration tests were conducted at 100 °C in an oven with temperature regulation and at reflux temperature, for 8 h in both cases. The objective of this optimization was the identification of the most reliable assay procedure in view of the large number of samples to be analyzed in the full study.

Oven migration testing was conducted, and the potential loss of simulant was taken into account due to the extended duration of the test (8 h) and the high temperature (100 °C), as well as the composition of the simulant containing 50 % EtOH (boiling point approximately 78 °C). Therefore, the following tests were conducted using both blanks and samples: (a) vials fully filled with simulant D1 and sealed with a SPME screw cap, (b) vials fully filled with simulant D1 and sealed with a cap, (c) vials with 18 mL of simulant D1, sealed with a SPME screw cap.

The reflux migration test involved the same sample preparation as for the oven test and maintained the reflux system for the duration of the 8 h test. Blanks of simulant were also prepared and simultaneously run. All samples were analyzed in triplicate to ensure repeatability.

To avoid overestimation of the migration, additional migration tests were conducted using 20 % EtOH as simulant in a set of samples. Since all the supplied silicone molds were meant to be used for food products such as bakery items, further testing was conducted using 3 % acetic acid as simulant and a set of samples were also tested at 100 °C for 4 h. All tests were done without washing the molds before the tests, to mimic what most of the users would do.

Chosen conditions were as following. Migration assays performed at 100 °C for 8 h in vials with 18 mL of simulant D1, sealed with a screw cap.

2.4. Migration assays

As shown in [Table 1](#), all molds were silicone monomaterials with different shape and size. Consequently, they posed a significant challenge for being tested by filling the molds and keeping them at high temperature over 4 or 8 h. As a result, it was determined to carry out the tests using total immersion in the simulant. Thus, the molds were cut in strips of 6 cm × 1 cm and immersed into the simulant for the selected time and temperature. Three independent replicates were tested in each case.

2.4.1. Specific migration

The specific migration tests were carried out by immersing a sample piece in a 20 mL vial of food simulant, according to the ratio 6 dm²/kg simulant already established for plastics (Regulation (EU) No 10/2011 ([European Union Commission Regulation EU, 2011](#)) and its amendments) in order to ensure comparable results. Then, silicone strips were immersed in 18 mL of gravimetrically controlled food simulant for conducting the migration tests in hermetic glass vials. The test was performed on a double-sided strip, allowing both sides of the material to come into contact. The study consisted of three sequential tests

performed at 100 °C for 8 h or alternatively at 100 °C for 4 h using UF110 oven from Memmert (Schwabach, Germany). The function of the fan was turned off.

Migration tests were carried out using 3 % acetic acid (simulant B), 20 % ethanol (simulant C) and 50 % (simulant D1) as food simulants and blank of simulants were prepared in each case by triplicate. Simulants B and C also in combination with D1 were used to simulate the preparation of dishes other than cakes in silicone baking pans. For instance, it has been taken into account addition of alcohol to dish, sauces with aqueous character, baking of processed cheese or preserved cheese in an aqueous medium (feta, mozzarella, and similar). After the 1st and 3rd exposure the samples were analyzed to detect and identify any volatile migrant. Since no specific regulation on permitted migration substances in silicone exists, annex I of plastics Regulation (EU) No 10/2011 ([European Union Commission Regulation EU, 2011](#)) was used indicating a kind of positive list of migrants. Solid phase microextraction coupled to gas chromatography-mass spectrometry (SPME-GC-MS) was used for this purpose. Three independent aliquots of each sample and simulant were analyzed.

Only a few samples produced a turbid and in some cases coloured solution after the specific migration test. Turbid solution refers to those that after 24 h in fridge had cloudiness which was visible to the naked eye after the first migration and was accompanied by a solid precipitation.

The global migration tests were performed only on the cloudy samples because, in principle, they were "releasing" material, and it would be very likely that they would not comply with the global migration limit.

2.4.2. Global migration

Global migration was tested by immersing selected samples in simulant D1. Only samples that were turbid in the specific migration assays were tested. After 8 h contact time at 100 °C, the samples were removed. The simulants were transferred to beakers, evaporated to dryness at 110 °C and weighed to constant weight. The global migration value was then calculated as the difference between the weight before and after evaporation of the simulant, after subtracting the simultaneously obtained results for the blank sample (pure simulant). The migration has been repeated for 4 h at 100 °C in case of samples exceeding overall migration limit (OML) of 60 mg/kg for 8 h at 100 °C.

2.5. Analysis by SPME-GC-MS

The ethanolic simulants after the migration tests, were analyzed by SPME-GC-MS. To optimize the maximum percent of EtOH in the analysis, various dilutions containing 5 %, 10 %, and 20 % of EtOH were done for three samples (M3, M19, and M20) from the extract obtained after the exposure (50 % EtOH). Optimal results were achieved with extracts diluted to 5 % EtOH.

Once optimized, the working conditions for screening by SPME-GC-MS analysis were as follows: SPME module (CTC Analytics Combi Pal auto sampler) with SPME fiber (DVB/CAR/PDMS), shaking at 500 rpm, incubation time of 2 min, temperature set at 80 °C, extraction time of 20 min, and a desorption time of 2 min ([Asensio et al., 2022](#)). Agilent 6809 N GC coupled to Agilent MS 5975B mass spectrometry detector was used, with an HP-5 capillary column (Agilent Technologies, Madrid, Spain) under the following oven program: 50 °C for 5 min, then ramped at 10 °C/min to 300 °C and held for 5 min. Acquisition was conducted in SCAN mode ($m/z = 50-800$). The volatile compounds were tentatively identified using spectrum libraries from the NIST Chemistry WebBook (NIST 2020 Mass Spectral Library) and WILEY present in the equipment's software with a ChemStation matching factor greater than 80% based on probability based matching algorithm. Some peaks were confirmed by commercially available pure standards. Furthermore, the retention index (RI) for volatile compounds other than siloxanes found in the samples was measured. This measurement utilized a standard set

of n-alkanes (C7–C40) and was executed under consistent chromatographic conditions. Three replicates of blanks were injected and if any volatile siloxanes were detected in the blanks, their areas were subtracted from the areas of volatile siloxanes in the samples. To perform quantitative analysis, calibration curves were prepared using these standards in 5% EtOH solution with a LOD of 0.00005–0.014 mg/kg (see [supplementary materials](#)).

If the standard corresponding to each identified compound was unavailable, the identified compound was semi-quantified using other standard of similar chemical structure for example hexadecanal has been quantified with undecanal.

2.6. Target analysis of phthalates by SPME-GC-MS

Phthalates were searched in purpose in all samples, as they could escape from the general screening when being present at low concentration. Thus, the phthalates shown in [Table 2](#) were analyzed in 20% and 50% ethanol simulants after the migration tests, both diluted to 5% EtOH. In addition, SCAN chromatograms of samples that had been already analyzed by SPME-GC-MS were extensively searched for the characteristic mass fragments of phthalates (e.g., $m/z = 149$).

2.7. Risk assessment

A risk assessment was conducted on the migrant compounds identified. Initially, the compounds were cross-checked versus the positive list provided in Regulation (EU) No 10/2011 ([European Union Commission Regulation EU, 2011](#)). The values recorded were then compared to their specific migration limits (SML). In the case of non-listed compounds, their tentative toxicological potential was classified using the threshold of toxicological concern (TTC) (Cramer's List) through the use of Toxtree_v3.1.0.1851® software. Cramer classifies all compounds based on their chemical structure into three categories: class I (low toxicity), class II (medium toxicity), and class III (high toxicity) and recommends maximum values for human exposure for each toxicity class. Thus, the estimated daily intake (EDI) values for class I, II, and III are 1.8, 0.54, and 0.09 mg per person per day, respectively. Considering the intake of 1 kg food/person/day, the recommended maximum migration for each class is: class I (1.8 mg/kg), class II (0.54 mg/kg), and class III (0.09 mg/kg) ([Koster et al., 2011](#); [Patlewicz et al., 2008](#)).

In the case of siloxanes, in Spain, the Royal Decree 847/2011 ([The Ministry of Health, 2011](#)) suggested a limit of 60 mg/kg for the sum of all cyclosiloxanes, as they are substances that do not have a specific migration limit.

2.8. Statistics

The average \pm standard uncertainty (U ($p < 0.05$)) was used to represent the results of global and specific migrations also on figures. Concentrations were expressed as mg/kg.

3. Results and discussion

3.1. Optimization of migration test conditions

The three samples (M3, M19, and M20) examined to optimize the

Table 2
Details of analyzed phthalates.

Phthalates	Target m/z	SML (mg/kg) (EU) 10/2011
diethyl phthalate	149/177	0.010
diisobutyl phthalate	149/223	0.010
dibutyl phthalate	149	0.30
benzyl butyl phthalate	57/91/149/205	30
bis(2-ethylhexyl) phthalate	149/167/279	5

migration test conditions did not show significant different experimental results when the tests were conducted in the oven or at reflux. However, conducting the migration test at reflux temperature leads to a substantial loss in simulant quantity after 8 h of testing, as well as significant variability. The best result of migration tests was achieved using vials containing 18 mL of simulant D1 and SPME screw caps.

The 5% EtOH employed for testing yielded satisfactory results, indicating the existence of numerous migrating compounds, mainly siloxanes and derivatives. Upon comparison, it was observed that decreasing % of EtOH, the equipment's sensitivity increased, leading to the decision to dilute the simulants (20% or 50% EtOH) up to 5% ethanol to be analyzed by SPME-GC-MS.

3.2. Global migration

The results of global migration, for the samples that showed turbidity after the migration assay in 50% EtOH at 100 °C for 8 h, are shown in [Fig. 1](#). Each baking mold sample is identified by a unique number and its country of origin. The OML established by EU is 60 mg/kg.

As shows [Fig. 1](#), samples M1 and M14 exceeded the global migration limit performed at 100 °C for 8 h. However, when these samples were exposed at 100 °C for 4 h the global migration was 8.22 ± 0.78 mg/kg and 15.00 ± 1.41 mg/kg for M1 and M14, respectively. When discussing baking molds, a prominent turbidity in a test solution indicates that there are numerous colloidal released from the mold. Such particles can migrate from molds, particularly under high temperature or specific baking conditions.

There are multiple reasons why elevated turbidity, what means a significant concentration of colloidal particles, can result in increased measurements of global migration. Among these reasons could be the conditions chosen for the migration tests, delimited by the type of simulant chosen (95% EtOH) that represents the fatty foods.

Firstly, the constituent material of certain baking molds may be susceptible to degradation and subsequent release of particles into baked products. It would be interesting to study in more detail if it is due to cross-link processes, ethanolysis or thermal stress. In turn, the movement of these particles can heighten the turbidity of any solution used to assess migration levels. Secondly, temperature sensitivity is another important factor to consider. Baking molds are subjected to high temperature that can intensify particle migration. If long periods at high temperature are applied, the migration is higher, as rising temperature can cause material breakdown and release of colloidal particles. Investigating the correlation between turbidity and migration from baking molds is crucial.

3.3. Screening analysis by SPME-GC-MS

Migration of volatile compounds were not detected (LODs = 0.00005–0.014 mg/kg) in the case of 3% acetic acid (simulant B) what means that the molds under study can be used in contact with acidic food at pH below 4.5. In the case of 20% EtOH (simulant C) migration of volatile compounds was neither detected. This means that the samples could be used in contact with foods with an alcohol or fat content up to 20% and those foods which contain a relevant amount of organic ingredients that render the food more lipophilic. The use of baking molds covers all these types of foods: from roast meats to pastries, cakes, etc. In the case of simulant D2 (95% EtOH), migration of volatile compounds were observed.

3.3.1. Siloxanes

[Figs. 2 and 3](#) show the quantitative values of total siloxanes from D4 to D10, derivatives of siloxanes and compounds containing silicon (Si) (from D4 to D12) after the first and third migration. Total siloxanes from D4 to D10 are specific cyclic siloxanes with ring sizes containing four to ten silicon atoms. Siloxane derivatives are compounds derived from siloxanes, including linear and branched structures containing silicon and

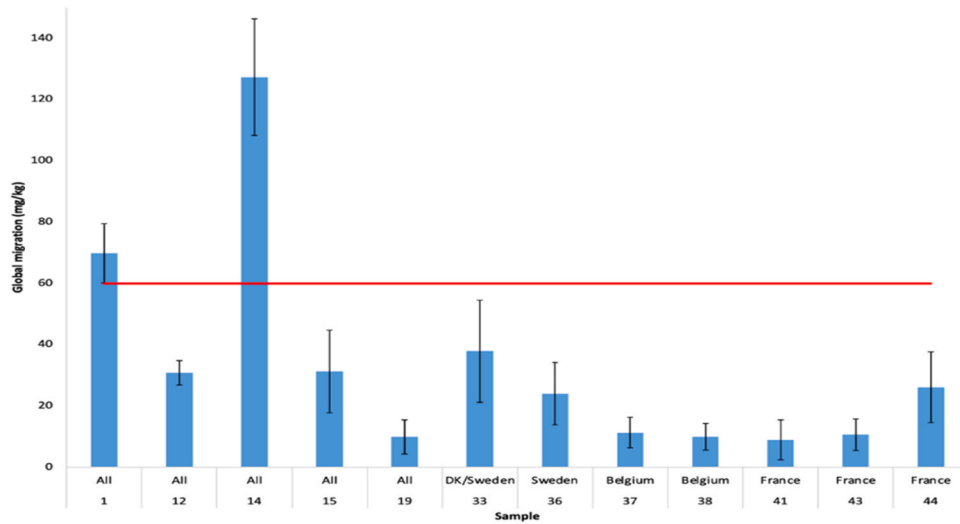


Fig. 1. Results of global migration (mean and standard deviation of triplicates), measured as gravimetric value of residue after evaporation, performed at 100 °C for 8 h expressed as mg/kg. Red line indicates OML.

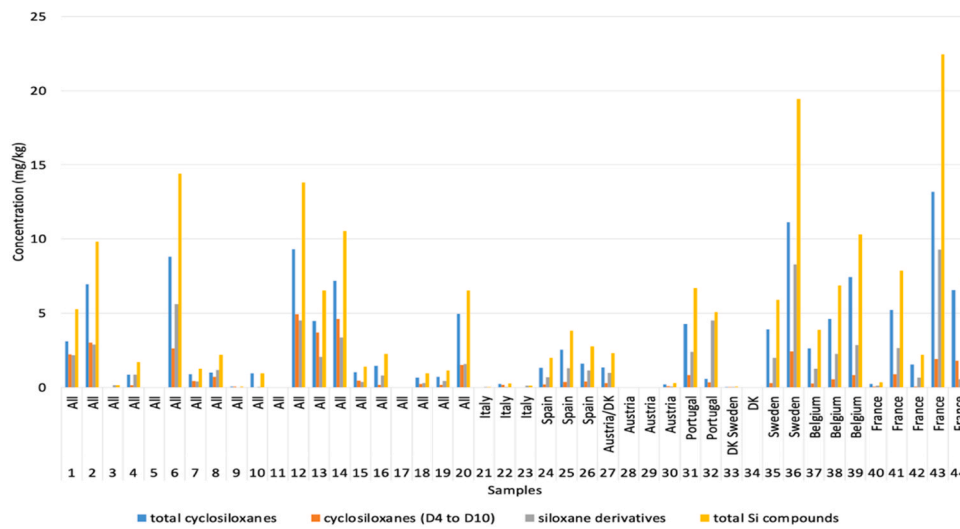


Fig. 2. Quantitative analysis of volatile siloxanes after first migration in 20% ethanol.

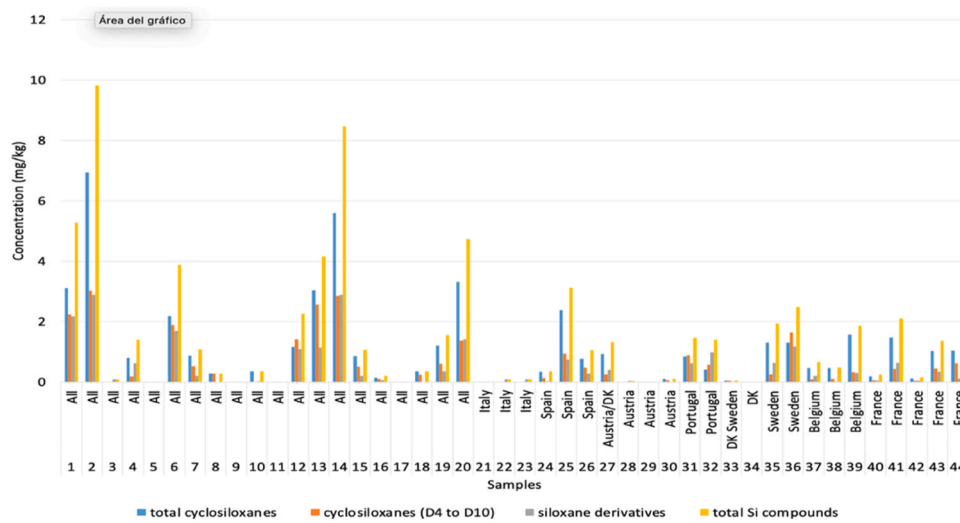


Fig. 3. Quantitative analysis of volatile siloxanes after third migration in 20% ethanol.

oxygen, but not necessarily in a cyclic form. They can also include functionalized siloxanes with additional chemical groups. While compounds containing silicon encompasses all compounds containing silicon, extending beyond just siloxanes. This includes any silicon-containing compound detected within the sample, whether cyclic, linear, or branched, and whether functionalized or not. The detailed concentrations can be found in [supplementary materials](#).

When examining the data of total cyclosiloxanes, it is clear that there is a wide range of variability in concentration among the samples. Some samples (e.g., samples 5, 9, 11 and 17) had no detectable levels of cyclosiloxanes, indicating either an absence of these compounds or levels below the detection limit (0.0010 mg/kg). In contrast, other samples have significantly high concentrations, indicating a significant presence or potential release of these compounds (e.g., samples 6, 12, 36 and 43).

The obtained concentrations of cyclosiloxanes (D4 to D10) can be divided into four groups as no detectable (LOD = 0.0010 mg/kg), very low level (< 0.5 mg/kg), low level (< 5 mg/kg), high level (> 5 mg/kg). It was checked that all samples with detected cyclosiloxanes (D4 to D10) below 5 mg/kg were made of platinum silicone. Exception are samples 3, 18 and 26 where the type of silicon was unknown. Platinum-cured silicone is preferred by the pharmaceutical and food industries. This type of silicone has superior elasticity and tear resistance, however, it's more difficult and expensive to produce, requiring high temperatures for curing and rapid molding after preparation ([Silicone Additives Market, 2020](#); [Health Public Committee, 2004](#)). Previous studies carried out with solid simulant (Tenax©) at high temperature revealed the important difference that exists in the migration of volatile compounds between molds that have been subjected to platinum-curing at high temperature, and that have a higher cost compared to cheaper molds that, as it turned out, had not been subjected to curing treatment ([Asensio et al., 2022](#)).

In addition, the data suggest that certain samples (e.g., samples 2 and 14 with very high 3rd migration) may be more prone to release or contain cyclosiloxanes than others. This could be due to differences in manufacturing, source of raw materials, or the long exposure of the samples at 100 °C. The presence of cyclosiloxanes, especially at varying concentrations, underscores the importance of understanding their origin and potential impact, especially if these samples are intended for sensitive applications such as food contact or medical use.

3.3.2. Phthalates

The comprehensive results of the migration of phthalates can be found in the [supplementary materials](#). For the first and third migration tests (20% and 50% EtOH), the concentrations of migrated phthalates were below the detection limits (0.0010 mg/kg) of the employed method. However, there was an exception for sample M19, where dibutyl phthalate was detected at concentrations of 0.27 ± 0.02 mg/kg and 0.18 ± 0.01 mg/kg over the first and third migrations in 50% EtOH, respectively. Consequently, all samples are in compliance with the EU's Specific Migration Limits (SMLs) for phthalates (0.3 mg/kg for dibutyl phthalate). Notably, the migration of dibutyl phthalate in sample M19 exhibited a decreasing trend. This is a positive indication, especially considering the potential health concerns associated with phthalate exposure.

3.3.3. Other volatile compounds

Analysis of volatile compounds different from siloxanes in the samples exposed to 50% EtOH (simulant D1) showed that some samples did not comply with Cramer thresholds in case of the study performed at 100 °C for 8 h. [Table 3](#) shows the list of volatile compounds identified by SPME-GC-MS excluding siloxanes and derivatives. The list of the samples in which the compounds were detected can be found in [supplementary materials](#). Moreover, [Fig. 4](#) shows the overlay of chromatograms corresponding to two different samples.

According to the results of qualitative analysis ([Table 3](#)), a wide

Table 3

List of detected volatile compounds other than siloxanes by SPME-GC-MS.

No	Compound	CAS number	RI experimental	RI literature *
1	undecanal	112-44-7	1312	1311
2	dodecanal	112-54-9	1413	1412
3	2,6-bis(1,1-dimethylethyl)-2,5-cyclohexadiene-1,4-dione	719-22-2	1468	1472
4	dodecanol	112-53-8	1479	1475
5	dibenzofuran	132-64-9	1536	1537
6	2,2,4-trimethyl-1,3-pentanediol diisobutyrate	6846-50-0	1592	1588
7	dodecanoic acid, 1-methyl-ethyl ester	10233-13-3	1619	1618
8	benzophenone	119-61-9	1645	1625
9	1,2,3-trimethyl-4-propenyl-naphthalene	26137-53-1	1664	not found
10	3,4-diethyl-1,1'-biphenyl (isomers)	61141-66-0	1687	1692
11	3,4-diethyl-1,1'-biphenyl (isomers)	61141-66-1	1696	1692
12	2,6-diisopropyl-naphthalene (DIPNs) (isomers)	24157-81-1	1723	1725
13	2,6-diisopropyl-naphthalene (DIPNs) (isomers)	24157-81-1	1731	1725
14	2,6-diisopropyl-naphthalene (DIPNs) (isomers)	24157-81-1	1737	1725
15	ethyl myristate	124-06-1	1787	1793
16	2-ethylhexyl salicylate	118-60-5	1810	1814
17	isopropyl myristate	110-27-0	1816	1817
18	hexadecanal	629-80-1	1816	1817
19	2,4-diphenyl-4-methyl-2(E)-pentene	22768-22-5	1841	1836
20	hexadecen-1-ol, trans-9-	64437-47-4	1882	1863
21	1-hexadecanol	36653-82-4	1883	1883
22	methyl palmitate	112-39-0	1924	1928
23	ethyl palmitate	628-97-7	1992	1994
24	isopropyl palmitate	142-91-6	2021	2011
25	hexadecanoic acid	57-10-3	2023	2024
26	octadecanal	638-66-4	2024	2033
27	1-octadecanol	112-92-5	2091	2090
28	9,12-octadecadienoic acid, methyl ester	2462-85-3	2098	2094
29	11-octadecenoic acid, methyl ester	52380-33-3	2104	2103
30	8-octadecenoic acid, methyl ester	2345-29-1	2113	2108
31	2(3H)-furanone, 5-dodecyl-dihydro-	730-46-1	2129	2120
32	heptadecanoic acid	506-12-7	2136	2086
33	ethyl stearate	111-61-5	2209	2199
34	octadecanoic acid	57-11-4	2214	2200
35	2(3H)-furanone, dihydro-5-tetradecyl-	502-26-1	2338	not found
36	methyl dehydroabietate	1235-74-1	2366	2360
37	oleamide	301-02-0	2382	2375

* Literature Kovatz indexes are from NIST webbook ([Silicone Additives Market, 2020](#)).

range of compounds (37 different volatile compounds) other than siloxanes were detected in samples of silicone molds. Most of the substances found are ubiquitous and thus are plausible as secondary contaminations to the materials tested. Aliphatic aldehydes such as undecanal, dodecanal, hexadecanal and octadecanal, which are often associated with fragrances or degradation products, were found. Alcohols and their related esters such as dodecanol, hexadecen-1-ol, and various myristate and palmitate derivatives were also detected. Aromatic compounds including dibenzofuran, benzophenone, and several isomers of diethyl biphenyl and diisopropyl-naphthalenes were present, suggesting potential aromatic additives or contaminants. Furanones,

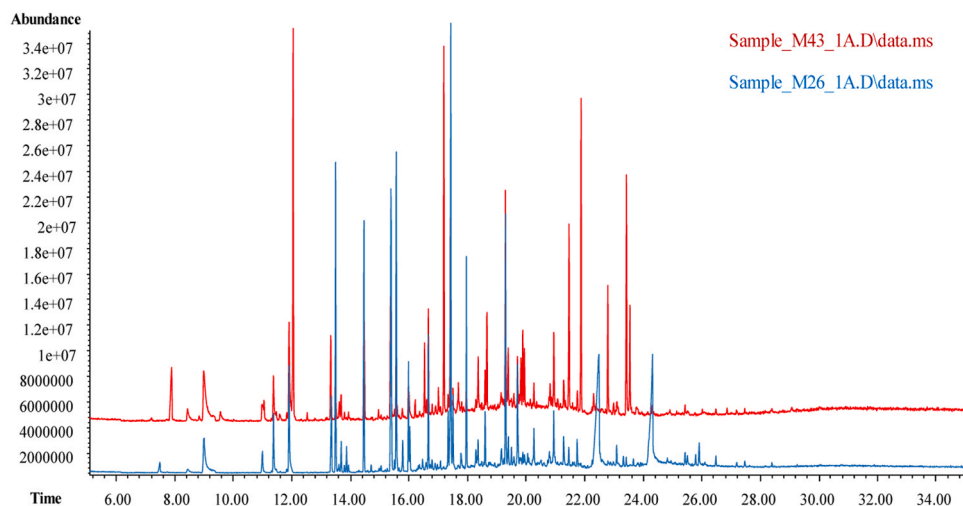


Fig. 4. Overlay SPME-GC/MS chromatograms of sample M26 (blue) and sample M43 (red), corresponding to the first migration.

specifically 5-dodecyl-dihydro-2(3H)-furanone and dihydro-5-tetradecyl-2(3H)-furanone, were identified and may be related to flavour or aroma compounds. The list also included several acids and their esters, such as dodecanoic acid and octadecanoic acid derivatives, which may indicate fatty substances or degradation products. The presence of these compounds provides information into the composition, potential additives or contaminants in the samples being tested. The compounds found, when placed in the context of polymer science, suggest different functional roles or origins. 2-ethylhexyl salicylate and 2,2,4-trimethyl-1,3-pentanediol diisobutyrate may act as plasticizers (Silicone Additives Market, 2020), with the former sometimes acting as a UV stabilizer in certain polymers to prevent degradation by sunlight. Benzophenone, another compound identified, is a common photoinitiator and also often used as a UV stabilizer in polymers. On the other hand, 2,6-bis(1,1-dimethylethyl)-2,5-cyclohexadiene-1,4-dione is a degradation compound from an antioxidant. Aliphatic aldehydes, such as undecanal, dodecanal and hexadecanal, and certain aromatic compounds, such as dibenzofuran, could either be residuals from the polymer manufacturing process or result from polymer chain degradation. Aldehydes are usually odorous compounds. Their presence may indicate either residual solvents or by-products from the synthesis or processing of the polymer.

Table 4 summarizes samples and volatile compounds that do not comply with their classification according to Cramer rules. Factor of exceedance (FE) was calculated by dividing concentration by Cramer limit. The detailed results for all samples can be found in supplementary materials. The results are presented as concentration minus Cramer (mg/kg) to show how much the limit was exceeded.

Compounds such as hexadecanal, octadecanal, trans-9-hexadecen-1-

ol, and 1-octadecanol exceeded Cramer thresholds or global migration for substances of very low relevance in some samples in case of third migration at 100 °C for 8 h. Nevertheless, specific migration has been repeated at 100 °C for 4 h for sample M7. Results indicate that in this case sample M7 comply with Cramer rules.

On the other hand, no data are available when checking the toxicity data of these compounds in the OpenFoodTox database (Chemical Hazards Database) of the European Food Safety Authority (EFSA) and the CompTox Chemicals Dashboard (CompTox Chemicals Dashboard from the U.S.) from the U.S. Environmental Protection Agency (EPA) there is no data available. Therefore, the structural simplicity of detected molecules and their classification may suggest minimal risk at typical exposure levels.

4. Conclusions and recommendations

Silicone molds are commonly used in conventional ovens at high temperature. According to the results shown in this study, it is recommended to use 50% ethanol, and increase the time of the exposure instead of increasing the temperature. In this study, 8 h were selected as the exposure time and some samples were also tested at 4 h, in both cases at 100 °C. Most of the samples released cyclic polysiloxanes and also some aldehydes. Concerning the migration of substances found, it can be confirmed that there is not safety concern, as all of them complied with the Royal Decree 847/2011 (The Ministry of Health, 2011) and with the recommendations of Council of Europe (Health Public Committee, 2004).

In the case of 3% acetic acid, no migration of volatile compounds was detected, which means that the tested molds can be used in contact with

Table 4

Summary of samples and volatile compounds that do not comply with Cramer rules or global migration in case of third migration in 50% ethanol at 100 °C for 8 h.

	hexadecanal (class I)	hexadecen-1-ol, trans-9- (class I)	Octadecanal (class I)	1-octadecanol (authorized without SML)
	Concentration mg/kg ± U (p < 0.05)			
		FE*	FE*	FE*
M1	29.94 ± 3.02	16.63		
M2	13.71 ± 4.55	7.62		
M7	8.55 ± 2.80	4.75		
M14			10.85 ± 0.99	6.03
M15	8.41 ± 2.78	4.67	3.96 ± 1.33	474.80 ± 28.66
M25	16.86 ± 0.36	9.37	8.63 ± 0.93	7.91
M26			6.22 ± 3.04	
M35			9.41 ± 2.25	
M38			5.81 ± 0.11	
M39	19.56 ± 6.06	10.87	3.23	

* Compound exceeded global migration limit (GML = 60 mg/kg). Factor of exceedances calculated as concentration/GML.

acidic foods with a pH below 4.5. All samples comply with the legislation in the case of volatile siloxanes.

Food simulant D1 (50% EtOH) is used for alcoholic foods with an alcohol content above 20% and for oil-in-water emulsions. Samples M1, M2, M7, M14, M15, M25, M26, M35, M38 and M39 exceeded recommended migration values for volatile compounds other than siloxanes after third migration in 50% EtOH at 100 °C for 8 h and therefore don't comply with Cramer thresholds. Nevertheless, migration has been repeated in case of sample M7 at 100 °C for 4 h and there were not any volatile compounds exceeding migration limits.

In the context of silicone molds, it is important to ensure that the silicone used is food grade and has undergone rigorous testing to ensure that it does not release harmful or undesirable compounds into the food. The migration of these compounds from silicone molds, especially when they exceed certain limits, raises concerns about the quality and safety of the silicone material used. It's critical to identify the source of these compounds, whether they are inherent to the silicone formulation, from additives or from external contamination.

Manufacturers should be aware of these potential migrations and may need to reformulate or refine the manufacturing process to reduce or eliminate the release of these compounds. And consumers should ensure that they are purchasing high-quality, food-grade silicone molds.

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CRedit authorship contribution statement

Cristina Nerín: Writing – review & editing, Project administration, Funding acquisition, Conceptualization. **Esther Asensio:** Writing – review & editing, Writing – original draft, Validation, Supervision, Resources, Project administration, Methodology, Investigation, Data curation, Conceptualization. **Lucía Aparicio:** Validation, Methodology, Investigation, Data curation. **Magdalena Wrona:** Writing – review & editing, Writing – original draft, Validation, Supervision, Methodology, Investigation, Data curation, Conceptualization. **Raquel Becerril:** Validation, Investigation, Formal analysis, Data curation. **Valeria Alloca:** Validation, Data curation, Conceptualization.

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.

Data availability

Data will be made available on request.

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Appendix A. Supporting information

Supplementary data associated with this article can be found in the online version at [doi:10.1016/j.fpsl.2024.101334](https://doi.org/10.1016/j.fpsl.2024.101334).

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