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**DTU Food**
National Food Institute

National Food Institute

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Tommy Licht Cederberg and Lisbeth Krüger Jensen

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Report August  2017

By Tommy Licht Cederberg and Lisbeth Krüger Jensen


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# Preface

This investigation was planned in cooperation with Julie Tesdal Håland, Norwegian Food Safety Authority (Mattilsynet), Chemical Safety and EEA Section.

The laboratory work and chemical analyses were performed by laboratory technician Marianne E. Jensen and laboratory engineer Lisbeth Krüger Jensen in cooperation with senior advisor Tommy Licht Cederberg.

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Lyngby, Denmark, August 24, 2017

Tommy Licht Cederberg
Senior Advisor

# Content

# Summary


Silicone is used in food contact materials due to its excellent physical and chemical properties. It is thermostable and flexible and is used in bakeware and kitchen utensils. Silicone is also used to coat paper to make it water and fat resistant.

There is no specific regulation in EU which covers silicone as food contact materials, but in Regulation 1935/2004 on materials intended to come into contact with food it is stated that materials should be manufactured so it do not transfer their constituents to food in quantities which could endanger human health.

Silicone may contain residual siloxane oligomers which might migrate to the food when the product is being used. DTU has proposed two action limits for low molecular weight siloxanes in food contact materials. For the sum of cyclic siloxanes D3 to D8 the limits are 12 mg/kg food for adults and 2 mg/kg food for children. For the sum of cyclic siloxanes D3 to D13 and linear siloxanes L3-L13 the limit is 60 mg/kg food.

In 49 samples of silicone products intended for food contact from the Norwegian markets content of siloxanes has been measured.

Coated paper for baking constituted 8 of the samples and in none of those samples siloxanes were found above the detection limits. In all of the 41 remaining samples siloxanes were found in content above the quantification limits. The siloxanes were predominately cyclic siloxanes. The types of products were baking moulds and mats, muffin cups, kitchen utensils, boxes and teats.

Compared to the proposed actions limits for the sum of D3 to D8 and for the sum of D3 to D13 plus L3 to L13, 24 of the samples exceeded these limits. However, the contents were determined by extraction of the total amount of the analysed siloxanes. After migration test to evaluate the migration of siloxanes into a food simulant it could be concluded, that none of the samples would exceed the action limits based on migration estimation.

The silicone product exhibited a wide range of siloxane concentrations and a hypothesis could be that the products with the highest siloxane content were not properly cured. Based on the available sample documentation obtained from the producers it was not possible to draw any conclusion about this aspect.

# 1. Background

Silicone is used to an increasing extent in food contact materials. Examples are baking moulds, kitchen utensils, teats and surface coating on baking and food paper. In bakeware silicone products can be made flexible and yet still able to retain their shape. Silicone is thermostable and chemically resistant. Paper for food contact can be coated with silicone in order to produce a surface which is water and fat resistant.

In contrast to plastic polymers that consist of carbon chains, silicone polymer has a skeleton of silicon and oxygen atoms. The individual building blocks (oligomers) are called siloxanes and the polymer is called silicones or polysiloxanes. The terms “siloxanes” and “silicones” are often used synonymously. The silicon and oxygen atoms can be arranged in linear or cyclic chains and siloxanes are characterised as being linear or cyclic.

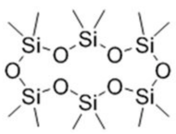
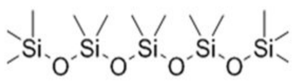
In silicones there may be a content of oligomers (siloxanes) which are residual content after polymerisation or chemical reaction compounds formed during the process. There is also the possibility that siloxanes are formed during the use of silicone products e.g. by repeated used of baking mould at high temperatures.

In this project samples of various types of consumer products of silicone were analysed for content of 11 linear and 11 cyclic siloxanes.

## 1.1 Nomenclature of siloxanes

The systematic names and chemical structures of the siloxanes analysed in this project are listed in Appendix B. In order to describe complicated siloxane polymers structures the silicon industry is using an abbreviated nomenclature based on structural units. Cyclic siloxanes are composed of a number of difunctional -O-SiR$_2$-O units and dodecamethyl-cyclohexasiloxane as an example is formed by the use of six of these units and is named D6 in a short hand notation (Table 1). Linear siloxanes is terminated by monofunctional R$_3$-Si-O- units and dodecamethyl-pentasiloxane as an example is formed by three D units and two M units and the proper short hand notation is MD3M. However, simple low molecular weight linear siloxanes is commonly named by capital letter L followed by the number of silicon atoms in the compound, i.e. L5 in this example.

Table 1. Example of short hand names of a cyclic and a linear siloxane.

| Systematic chemical name | Structure | Molecular formula | Functional units | Short hand name |
|---|---|---|---|---|
| Dodecamethyl-cyclohexasiloxane |  | $C_{12}H_{36}O_6Si_6$ | D6 | D6 |
| Dodecamethyl-pentasiloxane |  | $C_{12}H_{36}O_4Si_5$ | MD3M | L5 |

# 2. Regulation and action limits of siloxanes

## 2.1 Regulation

There is no specific EU legislation for food contact materials of silicone but Regulation 1935/2004 on materials and articles intended to come into contact with food covers all type of chemical materials (European Commission 2004). In article 3 in this Regulation it is stated that materials and articles shall be manufactured in compliance with good manufacturing practice so that, under normal and foreseeable conditions of use, they do not transfer their constituents to food in quantities which could endanger human health.

## 2.2 Action limits

No specific maximum limits exist for migration of chemical compounds from silicone products to food but DTU Food, National Food Institute has proposed action limits for low molecular weight siloxanes in food contact materials (DTU Food 2016b).

Table 2. Proposal for action limit for siloxanes in food contact materials with silicone.

| Siloxanes | Action limit mg/kg food |
|---|---|
| Sum of cyclic siloxanes D3-D8 | 12 (adult 70 kg)<br>2 (child 12 kg) |
| Sum of cyclic and linear siloxanes D3-D8 and L3-L13 | 60 |

The action limit for the sum of D3 to D8 is based on a toxicological 90 day dose-response study with D5 on rats, which showed an increased liver weight. It is estimated that the effect of D5 can be extended to include D3 to D8.

For low molecular linear siloxanes there is no available toxicological data to propose an action limit. It is estimated that linear siloxanes are not genotoxic and hence a lower limit for health effects exist.

In order to reduce any risk for exposure to other siloxanes than included in the sum of D3 to D8 in is proposed to use the total migration limit from EU Regulation 10/2011 of 60 mg/kg food to cover all the cyclic and linear siloxanes up to L13 and D13. L13 and D13 are just below the 1000 Dalton limit, which is the general limit for absorption of molecules in the gastrointestinal tract.

# 3. Sampling and analytical testing

## 3.1 Procedures for sampling

Samples of silicone food contact materials were taken at importers or at retail shops in Norway. The relevant types of samples were described as bakeware (e.g. for bread, pizza and muffins), silicone coated paper for baking, cakes or wrapping of food, kitchen utensils and teats for bottles. Sampling was distributed across three Norwegian Food Safety Authority regions: “Stor-Oslo”, “Øst” and “Sør og Vest”, and followed procedures by the Norwegian Food Safety Authority. The food inspectors from the regions forwarded the samples to DTU with the accompanying documentation.

## 3.2 Sampling period

The samples were taken out between March 31, 2016 and September 23, 2016 sent to DTU during the period May 30, 2016 and October 5, 2016.

## 3.3 Sample types

DTU received in total 50 samples. One sample of a box was made of polypropylene and was not analysed. The remaining 49 samples distributed between 6 types of food contact materials as shown in Table 3.

Table 3. Overview of type of samples taken for this project.

| **Sample type** | **Number of samples** |
|---|---|
| Baking paper | 8 |
| Baking mats | 3 |
| Baking moulds | 11 |
| Muffin cups (reusable) | 4 |
| Kitchen utensils | 11 |
| Boxes | 3 |
| Teats | 9 |
| **Total** | **49** |

## 3.4 Analytical results

Analytical certificates with results and assessment of results were sent to the Norwegian Food Safety Authority.

## 3.5 Analytical method used

An accredited analytical method developed at DTU was used (DTU Food 2016a). In this method an extraction of the total content of the analysed siloxanes in the sample is determined. The analytical principle is in brief that representative parts of the sample are cut into suitable pieces

with a total area of 6 $cm^2$, an internal analytical standard is added and the sample is extracted by the use of ethyl acetate in reflux for 1 hour. The content of siloxanes is determined by gas chromatography with mass spectrometric detection (GC-MS) and the use of electron ionisation (EI). The quantification is done by data collected in selection ions monitoring mode. GC-MS conditions are described in Appendix D. Analytical results are expressed in mg/food by applying the conventional surface to volume factor of 6 (1 kg of food is surrounded by 6 $dm^2$). For samples of teats the actual surface to volume factor is much lower and the results in mg/kg food are in this case calculated by using the measured food contact surface area of the individual teats and a volume of milk of either 150 ml for infants or 250 ml for toddlers in accordance to the intended use of the product.
Authentic analytical standards are only commercial available for a limited number of siloxanes. For this project seven standards were purchased from Sigma Aldrich. Four cyclic siloxanes: D3, D4, D5 and D6; and three linear siloxanes: L3, L4 and L5. For these seven siloxanes the mass spectrometric determination were done by monitoring of one quantification ion fragment and two verification fragments (see Appendix D, table D.1).

For siloxanes without authentic analytical standard tests were performed to show, that the mass spectrometric response factors were comparable for L5 compared to L6-L13 and for D6 compared to D7-D13. Thus it is possible to use the calibration curves and response factors obtained for L5 and D6, respectively, for the quantification of the linear and cyclic siloxanes without authentic standards. The masses of the ion fragments monitored for quantification of D7-D13 and L6-L13 is shown in Appendix D, table D2.

The analytical detection limit, LOD, and quantification limit, LOQ obtained for the individual cyclic and linear siloxanes determined in the method are listed in Appendix C.

The method is validated for determination of selected siloxanes in samples of silicones (e.g. bakeware and teats) and samples of paper coated with silicone (e.g. baking paper and paper used for wrapping of food).

## 3.6 Quality assurance

The Danish accreditation body (DANAK) supervises the chemical methods applied at the DTU Food – National Food Institute. Routines are established for daily quality control of the methods taken into consideration a suitable composition of the analytical batch with respect to number of samples that are analysed in multiplicity, laboratory and solvent blanks and control charts.

# 4. Results and discussion

Sample information and analytical results of content of siloxanes is shown in Appendix A.

In total 49 samples were analysed. Eight of the samples were different types of baking paper, all of which is paper coated with a thin layer of silicone. Countries of origin of these samples were Denmark, Germany, Norway and Sweden. In none of the samples siloxanes were found above the analytical detection limits.  The remaining 41 samples were diverse types of silicone products that have a varying degree of material (silicone) thickness. The categories are baking moulds, reusable muffin cups, kitchen utensils, boxes and teats. Most of the samples originated from China but also from Austria, Germany, Italy, Spain, Thailand, Taiwan, UK and USA. Nine samples were of unknown origin. In all of these samples siloxanes were detected above the analytical quantification limits. For 22 samples the content significantly exceed the proposed action limits for the sum of cyclic and linear siloxanes D3-D13 and L3-L13 (60 mg/kg food) and 18 of these samples also exceed the action limit for the sum of cyclic siloxanes D3-D8 (12 mg/kg food).  For samples of teats it is relevant to compare the content of the sum of cyclic siloxanes D3-D8 with the action limit calculated for children of 2 mg/kg food and two samples exceed this limit with a content of 2.9 and 5.3 mg/kg food respectively (assessed by using results calculated with real food contact condition).

In samples with detectable amount of siloxanes it is predominately cyclic siloxanes that are found and generally with increasing content from D3 to D13. Only a few samples had, in addition to cyclic siloxanes, a low amount of linear siloxanes.

The wall thickness of the silicone products was quite different but there is no obvious relation to the measured amount of siloxanes.

The samples were analysed by extraction of the total content of siloxanes from the silicone products and compliance assessment in relation to the action limits should be done with regards to the amount of siloxanes that migrates from the food contact material to the food at normal use of the product.

In order to evaluate to what extent siloxanes migrate from silicone products to food migration tests have been conducted on two selected samples with content of siloxanes above the action limits. The selected samples were a baking mould and a kitchen utensil (spoon) with content of siloxanes among the highest measured. Migration conditions were chosen from Regulation 10/2011 on plastic materials (European Commission 2011), that describes temperature and time parameters for use with migration test of food contact materials of plastic. In the absence of specific rules for silicone it is considered to be a reasonable choice. The food simulant was 95% ethanol which is generally a choice for simulation of migration of siloxanes to fatty foods and oils (Zhang, 2012; Helling, 2010). For articles intended for repeated use the migration test is conducted three times and the third migration result is to be used. The obtained results are listed in Table 4.

The migration tests showed that the contents of siloxanes migrating to the food simulant in both cases are reduced to a level which is not exceeding the action limits.

Based on the migration tests it has been predicted that none of the samples in the project exceeds the proposed action limits when judged in relation to content capable of migrating to the food.

Table 4. Results of migration test.

| Sample type | Sample ID | Test type | Sum of D3-D8 (mg/kg food) | Sum of D3-D8 and L3-l13 (mg/kg food) |
|---|---|---|---|---|
| Baking mould | K16-0818 | Total extraction | 350[c] | 700[c] |
| Baking mould | K16-0818 | Migration[a] | 0.41[d] | 1.3[d] |
| Kitchen utensil | K16-0813 | Total extraction | 570 | 1700 |
| Kitchen utensil | K16-0813 | Migration[b] | 13[d] | 37[d] |

[a] migration conditions: 95% ethanol, 100°C, 4 hours, result of third migration test

[b] migration conditions: 95% ethanol, 100°C, 0.5 hours, result of third migration test

[c] triple measurement

[d] double measurement

In the documentation accompanying the samples several of the producers are referring to that the silicone products have been cured at high temperature, e.g. in 4 hour at 200°C. The curing is done in order to enhance the property of the silicone material but it will also decrease the amount of residual siloxane oligomers etc. References to the German recommendation XV on silicones are frequent as well (BfR 2014). In this recommendation on food contact materials a maximum of 0.5% volatile organic and 0.5% extractable compounds are allowed to be released from silicone elastomers. This should also secure that the products have been cured (Lund and Petersen 2002).

The measured content of extractable siloxanes in the collected samples for this project has a very vide range. A hypothesis could be that the products with the highest levels of siloxanes have not been properly cured. However, it has not been possible to make any judgement on this based on the available accompanying sample documentation.

# 5. Assessment and conclusion

In 49 samples of silicone products intended for food contact from the Norwegian markets content of siloxanes has been measured.

Coated paper for baking constituted 8 of the samples and in none of those samples siloxanes were found above the detection limits. In all of the 41 remaining samples siloxanes were found in content above the quantification limits. The siloxanes were predominately cyclic siloxanes.

Compared to proposed actions limits from DTU for sum of D3 to D8 and for sum of D3 to D13 plus L3 to L13, 24 of the collected samples exceeded these limits. However, the contents were determined by extraction of the total amount of the analysed siloxanes. After migration test to evaluate the migration of siloxanes into a food simulant in could be concluded, that none of the samples would exceed the action limits based on migration estimation.

The silicone product exhibited a wide range of siloxane concentrations and a hypothesis could be that the products with the highest siloxane content were not properly cured. Based on the available sample documentation obtained from the producers it was not possible to draw any conclusion about this aspect.

# References

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# Appendix A Samples of silicone products

## A.1. Sample information and analytical results

| Sample type | Trade name | Sampling date | Country of origin | Sample ID DTU | Sample ID NFSA | Surface to volume ratio | Siloxanes Sum of D3-D8 (mg/kg food) | Siloxanes Sum of D3-D13 and L3-L13 (mg/kg food) |
|---|---|---|---|---|---|---|---|---|
| Baking paper | Greaseproof pizzapapir | 10-05-2016 | Norge | K16-0556 | 100516025937 | 6 | <LOD | <LOD |
| | Pizza og bakeark | 10-05-2016 | Norge | K16-0558 | 100516025892 | 6 | <LOD | <LOD |
| | Bakepapir rull | 10-05-2016 | Norge | K16-0559 | 100516025936 | 6 | <LOD | <LOD |
| | Bakepapir Silidor | 25-04-2016 | Sverige | K16-0562 | 2016/096161 1 | 6 | <LOD | <LOD |
| | Toppits bakplåtspapper med struktur, 16 ark | 11-05-2016 | Tyskland | K16-0563 | 2016/123525 2 | 6 | <LOD | <LOD |
| | Unik bakepapir | 11-05-2016 | Danmark | K16-0564 | 2016/123525 3 | 6 | <LOD | <LOD |
| | Bakepapir, ark | 31-03-2016 | Danmark | K16-0582 | 10616029824 | 6 | <LOD | <LOD |
| | Bakepapir, ark med silikon | 05-04-2016 | Tyskland | K16-0585 | 10616029793 | 6 | <LOD | <LOD |
| Baking mats | Bakematte | 11-05-2016 | Thailand | K16-0575 | 2016/106509 6 - 802.330-72 | 6 | 0.14 | 3.7 |
| | Makronmatte | 27-05-2016 | Kina | K16-0576 | 2016/10658 9 | 6 | 0.58; 2.2 | 24; 100 |
| | Silikon bakeunderlag | 31-03-2016 | Kina | K16-0583 | 10616029825 | 6 | 0.32 | 17 |
| Baking moulds | Brødbaker i silikon | 24-05-2016 | Spanien | K16-0560 | 260516028727 | 6 | 6.3 | 24 |
| | Brødform, silikon | 24-05-2016 | Kina | K16-0568 | 2016/123812 7 | 6 | 8.8 | 110 |
| | Silikonform Ugle | 11-05-2016 | Kina | K16-0569 | 2016/105909 1 | 6 | 1.5 | 86 |
| | Kakeform hjerte | 11-05-2016 | Kina | K16-0570 | 2016/106509 6 | 6 | 4.1 | 370 |
| | Brødform | 27-05-2016 | Kina | K16-0577 | 2016/10658 10 | 6 | 0.31 | 6.8 |
| | Kakeform | 13-05-2016 | | K16-0579 | 2016/115459 - 240516028233 | 6 | 100 | 630 |
| | Is form | 30-05-2016 | | K16-0581 | 2016/117835 - 260516028635 | 6 | 0.85 | 12 |
| | Daisy Pops Silicone Mold | 11-05-2016 | Kina | K16-0586 | 2016/105812 5 | 6 | 580 | 1300 |
| | Kakeform Happy Love | 23-09-2016 | Italien | K16-0817 | 2016/196841 6 | 6 | 0.37 | 11 |
| | Makronmatte Rosa 6 stk | 23-09-2016 | Kina | K16-0818 | 2016/196841 7 | 6 | 330;340;380 | 670;690;740 |
| | Skje-form Rød jul | 23-09-2016 | Kina | K16-0819 | 2016/196841 8 | 6 | 82 | 570 |
| Muffin cups (reusable) | Muffinsform, art.85-4903 blomsterkrukke/potte silikon | 19-05-2016 | Kina | K16-0566 | 2016/123772 5 | 6 | 91;96;96 | 590;640;630 |
| | Muffinsform 12 stk, art.85-4901 blomst rosa farge, silikon | 19-05-2016 | Kina | K16-0567 | 2016/123772 6 | 6 | 7.8 | 83 |
| | Muffinsform | 11-05-2016 | Thailand | K16-0574 | 2016/106509 6 - 402.566.16 | 6 | 1.1 | 5.5 |
| | Muffinsform 12 stk, | 23-09-2016 | | K16-0815 | 2016/197249 4 | 6 | 7.8 | 22 |

Table continued…

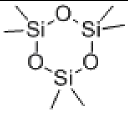
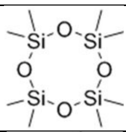
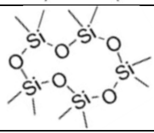
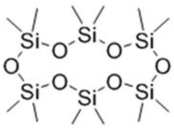
| Sample type | Trade name | Sampling date | Country of origin | Sample ID DTU | Sample ID NFSA | Surface to volume ratio | Siloxanes Sum of D3-D8 (mg/kg food) | Siloxanes Sum of D3-D13 and L3-L13 (mg/kg food) |
|---|---|---|---|---|---|---|---|---|
| Kitchen utensils | Røreredskap i silicon | 24-05-2016 | Kina | K16-0561 | 260516028683 | 6 | 150 | 670 |
| | Unik rørskje silikon | 13-05-2016 | Kina | K16-0565 | 2016/123725 4 | 6 | 63 | 340 |
| | Slikkepott grå | 11-05-2016 | Kina | K16-0571 | 2016/105909 2 | 6 | 360 | 1500 |
| | Trakt, sett med 3 | 11-05-2016 | Kina | K16-0572 | 2016/105909 3 | 6 | 1.9 | 12 |
| | Deigskrape | 11-05-2016 | Kina | K16-0573 | 2016/105812 4 | 6 | 760 | 2000 |
| | Måleskje | 30-05-2016 | | K16-0580 | 2016/117835 - 300516029331 | 6 | 64 | 690 |
| | Suppeøse, silikon | 01-04-2016 | Kina | K16-0584 | 10616029802 | 6 | 30;33;40 | 370;400;350 |
| | Silikonepensel | 23-09-2016 | | K16-0812 | 2016/197249 1 | 6 | 100 | 450 |
| | Røreskje blå indigo | 23-09-2016 | | K16-0813 | 2016/197249 2 | 6 | 570 | 1700 |
| | Stekespade | 23-09-2016 | | K16-0814 | 2016/197249 3 | 6 | 290 | 1100 |
| | Slikkepott | 23-09-2016 | | K16-0816 | 2016/197249 5 | 6 | 100 | 410 |
| Boxes | Matboks i silikon | 10-05-2016 | Kina | K16-0557 | 100516025891 | 6 | 200 | 910 |
| | Plastboks m/lokk | 13-05-2016 | | K16-0578 | 2016/115459 - 240516028199 | 6 | n.a | n.a |
| | Compleat foodbag matboks | 23-09-2016 | Kina | K16-0820 | 2016/197018 9 | 6 | 170 | 410 |
| | Compleat foodskin matboks | 23-09-2016 | Taiwan | K16-0821 | 2016/197018 10 | 6 | 200 | 340 |
| Teats | Philips Avent natural | 30-08-2016 | England | K16-0803 | 2016/206415 1 | 0.8 | 0.86;0.60;0.58 | 7.1;4.3;4.3 |
| | MAM teat 2 | 30-08-2016 | Østrig | K16-0804 | 2016/206415 2 | 1.0 | 0.14 | 0.41 |
| | Tommee Tippee | 30-08-2016 | Kina | K16-0805 | 2016/206498 3 | 1.0 | 5.3 | 19 |
| | Dr.Brown's natural | 30-08-2016 | USA | K16-0806 | 2016/206525 4 | 0.7 | 0.92 | 0.99 |
| | Munchkin Latch | 21-09-2016 | Kina | K16-0807 | 2016/206616 5 | 1.5 | 2.9 | 34 |
| | Esska silicon | 21-09-2016 | | K16-0808 | 2016/206616 6 | 0.4 | 0.14 | 0.88 |
| | Medela smokk | 21-09-2016 | | K16-0809 | 2016/206616 7 | 0.7 | 0.01 | 0.01 |
| | NUK first choise | 21-09-2016 | Tyskland | K16-0810 | 2016/206646 8 | 0.9 | 0.05 | 0.35 |
| | Twistshake antikolikk | 21-09-2016 | Kina | K16-0811 | 2016/206646 9 | 0.8 | 0.69 | 8.4 |

<LOD: below detecion limits see Appendix C

n.a.: not analysed

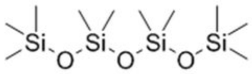
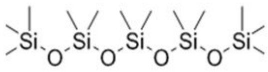
# Appendix B  Names and chemical information of siloxanes determined

## B.1.  Cyclic siloxanes

| ID | Compound | Structure | Molecular formula | CAS no. | Molecular weight (g/mol) | Boiling point |
|---|---|---|---|---|---|---|
| D3* | Hexamethyl-cyclotrisiloxane |  | $C_6H_{18}O_3Si_3$ | 541-05-9 | 222,06 | 134 °C |
| D4* | Octamethyl-cyclotetrasiloxane |  | $C_8H_{24}O_4Si_4$ | 556-67-2 | 296,62 | 175 °C |
| D5* | Decamethyl-cyclopentasiloxane |  | $C_{10}H_{30}O_5Si_5$ | 541-02-6 | 370,77 | 210 °C |
| D6* | Dodecamethyl-cyclohexasiloxane |  | $C_{12}H_{36}O_6Si_6$ | 540-97-6 | 444,92 | 245 °C |
| D7 | Tetradecamethyl-cycloheptasiloxane | See above | $C_{14}H_{42}O_7Si_7$ | 107-50-6 | 519.08 | |
| D8 | Hexadecamethyl-cyclooctasiloxane | See above | $C_{16}H_{48}O_8Si_8$ | 556-68-3 | 593.23 | |
| D9 | Octadecamethyl-cyclononasiloxane | See above | $C_{18}H_{54}O_9Si_9$ | 556-71-8 | 667.39 | |
| D10 | Eicosamethyl-cyclodecasiloxane | See above | $C_{20}H_{60}O_{10}Si_{10}$ | 18772-36-6 | 741.54 | |
| D11 | Docosamethyl-cycloundecasiloxane | See above | $C_{22}H_{66}O_{11}Si_{11}$ | 18766-38-6 | 815.69 | |
| D12 | Tetracosamethyl-cyclododecasiloxane | See above | $C_{24}H_{72}O_{12}Si_{12}$ | 18919-94-3 | 889.85 | |
| D13 | Hexacosamethyl-cyclotridecasiloxane | See above | $C_{26}H_{78}O_{13}Si_{13}$ | 23732-94-7 | 964.00 | |

*Compound with authentic standard available

## B.2. Linear siloxanes

| ID | Compound | Structure | Molecular formula | CAS no. | Molecular weight (g/mol) | Boiling point |
|---|---|---|---|---|---|---|
| L3* | Octamethyl-trisiloxane |  | $C_8H_{24}O_2Si_3$ | 107-51-7 | 236,53 | 153 °C |
| L4* | Decamethyl-tetrasiloxane |  | $C_{10}H_{30}O_3Si_4$ | 141-62-8 | 310,69 | 194 °C |
| L5* | Dodecamethyl-pentasiloxane |  | $C_{12}H_{36}O_4Si_5$ | 141-63-9 | 384,84 | 230 °C |
| L6 | Tetradecamethyl-hexasiloxane | See above | $C_{14}H_{42}O_5Si_6$ | 107-52-8 | 458.99 | |
| L7 | Hexadecamethyl-heptasiloxane | See above | $C_{16}H_{48}O_6Si_7$ | 541-01-5 | 533.14 | |
| L8 | Octadecamthyl-octasiloxane | See above | $C_{18}H_{54}O_7Si_8$ | 556-69-4 | 607.30 | |
| L9 | Eicosamethyl-nonasiloxane | See above | $C_{20}H_{60}O_8Si_9$ | 2652-13-3 | 681.46 | |
| L10 | Docosamethyl-decasiloxane | See above | $C_{22}H_{66}O_9Si_{10}$ | 556-70-7 | 755.61 | |
| L11 | Tetracosamethyl-undecasiloxane | See above | $C_{24}H_{72}O_{10}Si_{11}$ | 107-53-9 | 829.76 | |
| L12 | Hexacosamethyl-dodecasiloxane | See above | $C_{26}H_{78}O_{11}Si_{12}$ | 2471-08-1 | 903.92 | |
| L13 | Octacosamethyl-tridecasiloxane | See above | $C_{28}H_{84}O_{12}Si_{13}$ | 2471-09-2 | 978.07 | |

*Compound with authentic standard available

# Appendix C Analytical detection limits (LOD) and quantification limits (LOQ)

| Cyclic (D) and linear (L) siloxanes | LOD | LOQ |
|---|---|---|
| Hexamethylcyclotrisiloxane (D3) | <0.17 | <0.58 |
| Octamethylcyclotetrasiloxane (D4) | <0.056 | <0.19 |
| Decamethylcyclopentasiloxane (D5) | <0.026 | <0.088 |
| Dodecamethylcyclohexasiloxane (D6) | <0.007 | <0.025 |
| Tetradecamethyl-cycloheptasiloxane (D7) | <0.036 | <0.12 |
| Hexadecamethyl-cyclooctasiloxane (D8) | <0.036 | <0.12 |
| Octadecamethyl-cyclononasiloxane (D9) | <0.036 | <0.12 |
| Eicosamethyl-cyclodecasiloxane (D10) | <0.036 | <0.12 |
| Docosamethyl-cycloundecasiloxane (D11) | <0.036 | <0.12 |
| Tetracosamethyl-cyclododecasiloxane (D12) | <0.036 | <0.12 |
| Hexacosamethyl-cyclotridecasiloxane (D13) | <0.036 | <0.12 |
| Octamethyltrisiloxane (L3) | <0.10 | <0.35 |
| Decamethyltetrasiloxane (L4) | <0.009 | <0.030 |
| Dodecamethylpentasiloxane (L5) | <0.006 | <0.022 |
| Tetradecamethyl-hexasiloxane (L6) | <0.006 | <0.022 |
| Hexadecamethyl-heptasiloxane (L7) | <0.006 | <0.022 |
| Octadecamthyl-octasiloxane (L8) | <0.006 | <0.022 |
| Eicosamethyl-nonasiloxane (L9) | <0.006 | <0.022 |
| Docosamethyl-decasiloxane (L10) | <0.006 | <0.022 |
| Tetracosamethyl-undecasiloxane (L11) | <0.006 | <0.022 |
| Hexacosamethyl-dodecasiloxane (L12) | <0.006 | <0.022 |
| Octacosamethyl-tridecasiloxane (L13) | <0.006 | <0.022 |

Unit: mg/kg food

# Appendix D Analytical GC-MS conditions

## D.1. GC-MS setup

GC-MS: Agilent 6890A Plus.

GC-column: DB5-MS, 30 meter, i.d. 0.25 mm, film thickness 0.25 µm.

Injection: 1 µl splitless, split time 1 min.

Carrier gas: Helium with constant flow 37 cm/sec.
Oven program: 50°C for 3 min., 10°C/min. until 140°C, holding time 0 min, 40°C/min. until 300°C.

## D.2. Monitored ion fragments for siloxanes with authentic standards:D3-D6 and L3-L5

| Compound | RT (min) | Quantification mass (m/z) | Verification Q1 (m/z) | Verification Q2 (m/z) |
|---|---|---|---|---|
| D3 | 5.6 | 207 | 191 | 133 |
| L3 | 6.6 | 221 | 222 | 205 |
| D4 | 8.6 | 281 | 282 | 283 |
| L4 | 9.7 | 207 | 208 | 295 |
| D5 | 11.1 | 355 | 267 | 356 |
| Internal std. | 11.5 | 281 | 147 | 369 |
| L5 | 12.3 | 281 | 147 | 369 |
| D6 | 13.5 | 341 | 429 | 325 |

## D.3. Monitored ion fragments for quantification of D7-D13 and L6-L13

| Compound | RT (min) | Masses for calculation of sum areas |
|---|---|---|
| L6 | 14.5 | 73,147,221 |
| D7 | 15.2 | 73,147,327,415 |
| L7 | 15.7 | 73,147,221,295 |
| D8 | 16.1 | 73,147,221,355 |
| L8 | 16.4 | 73,147,221,295 |
| D9 | 16.8 | 73,147,221,355 |
| L9 | 16.9 | 73,147,221,295 |
| D10 | 17.2 | 73,147,221,355 |
| L10 | 17.4 | 73,147,221,295 |
| D11 | 17.6 | 73,147,221,355 |
| L11 | 17.9 | 73,147,221,295 |
| D12 | 18.0 | 73,147,221,355 |
| L12 | 18.2 | 73,147,221,295 |
| D13 | 18.4 | 73,147,221,355 |
| L13 | 18.6 | 73,147,221,295 |

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