Substantial Release of Silicones from Household Items and Baby Articles Analyzed by Direct Analysis in Real Time–Mass Spectrometry

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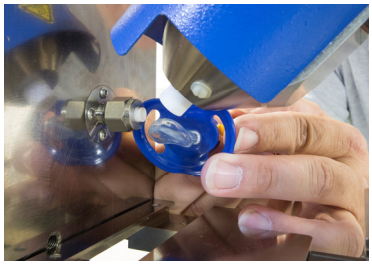
Topic of this Poster

- The release of low molecular weight silicone oligomers (polydimethylsiloxanes, PDMS) from articles of daily use such as flexible silicone baking molds, beakers, watch bands, pacifiers, nipples, and teething rings has been analyzed by direct analysis in real time (DART) [1–3] combined with a Fourier transform ion cyclotron resonance (FT-ICR) mass spectrometer.
- The substantial release of silicones at elevated temperatures within seconds indicates a potential health hazard from daily use of such silicone rubber items.
- Thus, a substantial dose of silicones may be taken up by humans, in particular during elongated exposure under extracting conditions as in case of pacifiers or teething rings or when used at elevated temperature as is the case with baking molds.
- Here, the use of DART-MS is demonstrated as a rapid screening technique for articles of daily use to assess their tendency to release silicones.

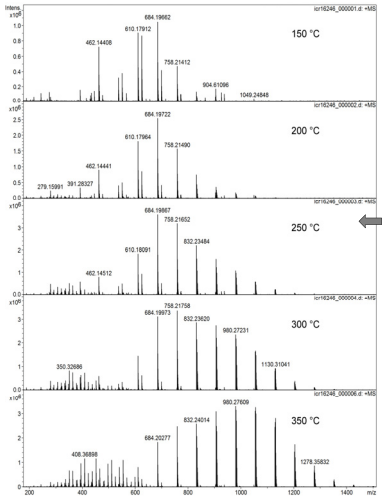
Experimental



A pacifier is being exposed to DART gas at 300 °C. (A photograph of the surface of the same object after three repeat runs is shown below.)

Experiments were performed using an Apex-Qe FT-ICR instrument (Bruker Daltonik). A DART-SVP ionization source (IonSense) was mounted at an angle of 45° relative to the axis of the ceramics tube of the Vapur-Interface. The mounting was recessed by 20 mm and the source lifted by 6 mm. Items were positioned halfway between helium exit and capillary entrance and exposed to the ionizing gas. Ions were accumulated for 1.0 s prior to ICR mass analysis. Ions were excited and detected using standard setting from previous DART work [4–6]. Broadband spectra were acquired with 1 M data points. Per spectrum, 16 transients were accumulated. Initial positive-ion mode mass calibration was established in DART mode using either silicone oil [4] or an ionic liquid [6].

Standardized DART Gas Temperature

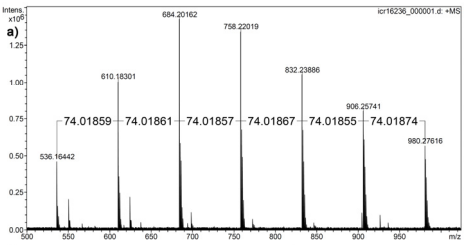


After screening the DART gas temperature in the range of 150 to 350 °C, a standard temperature of 300 °C was defined and applied to analyze all silicone rubber articles.

Above: Collection of articles belonging to different groups of application and supplied by various manufacturers.

Left: DART spectra of a Kaiser rectangular baking mold as obtained upon exposure to DART gas at 150 to 350 °C. For comparison of all articles, a standard of 300 °C was set.

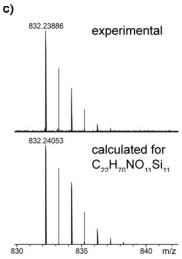
Identification of Silicones



b)

Meas. m/z	Formula	m/z	err [ppm]
536.16442	C 14 H 46 N O 7 Si 7	536.16536	1.8
610.18301	C 17 H 48 N O 11 Si 6	610.18375	1.2
	C 16 H 52 N O 8 Si 8	610.18416	1.9
684.20162	C 19 H 54 N O 12 Si 7	684.20254	1.3
	C 18 H 58 N O 9 Si 9	684.20295	1.9
758.22019	C 25 H 56 N O 12 Si 7	758.21819	-2.6
	C 21 H 60 N O 13 Si 8	758.22133	1.5
	C 24 H 60 N O 9 Si 9	758.21860	-2.1
	C 20 H 64 N O 10 Si 10	758.22174	2.0
	C 23 H 64 N O 6 Si 11	758.21901	-1.6
	C 19 H 68 N O 7 Si 12	758.22215	2.6
832.23886	C 27 H 62 N O 13 Si 8	832.23698	-2.3
	C 23 H 66 N O 14 Si 9	832.24012	1.5
	C 26 H 66 N O 10 Si 10	832.23739	-1.8
	C 22 H 70 N O 11 Si 11	832.24053	2.0
	C 25 H 70 N O 7 Si 12	832.23780	-1.3
	C 21 H 74 N O 8 Si 13	832.24094	2.5
906.25741	C 29 H 68 N O 14 Si 9	906.25577	-1.8
	C 28 H 72 N O 11 Si 11	906.25618	-1.4
	C 24 H 76 N O 12 Si 12	906.25932	2.1
	C 27 H 76 N O 8 Si 13	906.25659	-0.9
	C 23 H 80 N O 9 Si 14	906.25973	2.6
980.27616	C 30 H 78 N O 12 Si 12	980.27497	-1.2
	C 26 H 82 N O 13 Si 13	980.27811	2.0
	C 29 H 82 N O 9 Si 14	980.27538	-0.8

c)



- The signals belong to a single homologous series exhibiting a mass difference of 74.0188 u (calc. value), characteristic of $(CH_3)_2SiO$ units (**a**).
- The identification of silicones is further supported by equal appearance of spectra obtained from silicone septa or silicone oil.
- Silicone ionic compositions are verified by accurate mass measurement based on an independent external mass calibration (mass accuracy ≈ 2 ppm up to *m/z* 1000) [4, 5]. PDMS ions have equal number of Si and O atoms. They correspond to ammonium adduct ions, hence one nitrogen is contained (**b**).
- Isotopic patterns of all signal reveal numerous Si atoms (**c**).

Partial DART spectrum of a Pavoni braided ring baking mold at 300 °C with the mass differences annotated between adjacent peaks. The PDMS ionic formulas are marked in the list. The isotopic pattern of the signal at *m/z* 832.2388 is compared to the theoretical pattern.

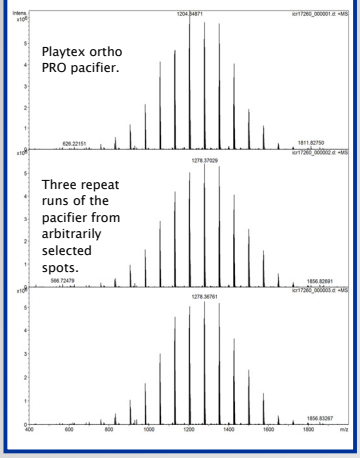
Reproducibility

It may be argued that the exact position and orientation of the items subjected to DART analysis are critical for the resulting spectra.

The reproducibility has therefore been tested by repeatedly measuring the same item. For each run, the item has been manually held in the ionization zone of the DART interface (photograph top right).

The spectra are from three repeated runs of a Playtex ortho PRO pacifier. There is no noteworthy effect on the resulting spectra neither in ion distribution nor in abundance.

Minor variation in angle and distances to ionization source and entrance capillary are easily tolerated.



Conclusions

- DART-MS is very sensitive for the analysis of silicones.
- DART-FT-ICR-MS can be used to analyze silicone (PDMS) release from articles of daily use.
- The substantial release of silicones from articles of daily use indicates a potential health hazard.
- All articles are equally bad and release lots of PDMS [7].
- DART may be useful for similar applications, e.g., to breast implants or food after having been in contact with silicone rubber.

Vendors

The items were obtained from different sources. Baking molds were from the author's household and have had multiple uses prior to DART analysis. Pacifiers, nipples, and other articles were purchased in Lorsch, Germany or in Baltimore, MD. Silicone septa were taken from stock in the laboratory.

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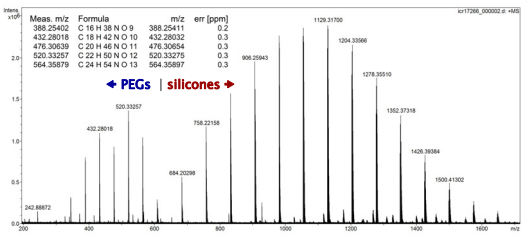
No Surface Damages

No surfaces damages or discoloration can be seen. Surface of a Playtex pacifier after three DART runs at 300 °C.

Exposure of a pacifier, a baking mold or other silicone rubber items to the DART gas at 300 °C does not really affect the surface integrity. Thus, the release of medium molecular weight silicones is not the consequence of major decomposition due to harsh conditions. Baking molds in particular are explicitly specified to resist up to 280 °C.

Bold statement on a Pavoni braided ring baking mold: "Heat resistant to 536 F (280 °C)". Enjoy your cake!

Release of Additional Compounds



Meas. m/z	Formula	m/z	err [ppm]
388.25402	C 16 H 38 N O 9	388.25411	0.2
432.28018	C 18 H 42 N O 10	432.28032	0.3
476.30639	C 20 H 46 N O 11	476.30654	0.3
520.33257	C 22 H 50 N O 12	520.33275	0.3
564.35879	C 24 H 54 N O 13	564.35897	0.3

NUK pacifier, DART gas at 300 °C. Here, PEGs in the range of MW 300–600 u are released in addition to silicones.

DART-FT-ICR spectrum of a NUK pacifier reveals the release of some low-mass polyethylene glycols that are detected as $[PEG+NH_4]^+$ ions. This spectrum has internally been recalibrated on silicone signals in the range of *m/z* 684 to 1202 according to the procedure in Ref. [4] prior to formula assignment to the additional compounds. Other occasionally occurring additives are plasticizers, for example.

References

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