Revision: June 2021

Testing instruction TEGEWA method – quantitative determination of D4 in chemicals

1. General Information

Purpose: Determination of cyclic siloxanes (i.a. D4) in silicon oils or aqueous silicone emulsions

Scope: Applicable for chemicals

Measurement principle: Quantitative gas chromatographic determination of D4, D5 and D6 in chemicals

Tasks and responsibilities: CAL

Internal method reference:

2. Instruments and reagents

Instruments	Description	Possible Supplier
GC-MS	**Agilent 6890N, MS5973 / Gerstel MPS2**	**Agilent / Gerstel**
Analytical balance	**Accurate to 0.1 mg**	**Mettler-Toledo**
Volumetric Flasks	**10 ml**	**VWR**
Ultrasonic bath		
HS-vials with septum	**20 ml**	**VWR**
Pipettes	**1000 / 500 / 100 / 50 µl**	**Eppendorff**
Syringe PTFE-filter	**SRP15 (0.45 µm)**	**Satorius**
Disposable syringe	**2 ml**	
GC-Vials	**2 ml**	

Reagents	Description	Possible Supplier
Octamethylcyclotetrasiloxane CAS 556-67-2 (D4-Siloxane)		**Merck**
Dodecamethylpentasiloxane CAS 141-63-9 (lin. D5-Siloxane)		**Sigma Aldrich**
Decamethylcyclopentasiloxane CAS 541-02-6 (cycl. D5-Siloxan)		**Merck or Sigma Aldrich**
Dodecamethylcyclohexasiloxane CAS 540-97-6 (D6-Siloxan)		**Merck or Sigma Aldrich**
Chloroform [1]		**VWR Chemicals**
Sodium sulfate (anhydrous) 98.5-101.0%		**VWR Chemicals**
Magnesium sulfate (anhydrous) 99-100.5% (Magnesium sulfate, ⩾98.0%)		**VWR Chemicals (VWR)**
Acetic acid (100%)		**VWR Chemicals**

[1] A test of different solvents was performed, but the reproducibility of the test results with solvents other than chloroform was not given.

3. Test procedure(s)

Sample preparation:

a. <u>For samples which are clearly soluble in chloroform (e.g., silicone oils):</u>

- Weigh in 0.3 g – 0.5 g (with an accuracy of 1 mg) into a 10 ml volumetric flask
- Add 0.1 ml of acetic acid (100%) and
- Fill-up to the mark with chloroform and homogenize

This solution is transferred into a 2 ml GC-vial.

b. <u>For water-containing samples:</u>

Approximately 8 g of a 1:1 mixture (w/w) of sodium sulfate (anhydrous) and magnesium sulfate (anhydrous) are placed into a 20 ml HS-vial.

- approximately 1 g, with an accuracy of 1 mg, of the sample is weighed in.
- Add 0.1 ml of acetic acid (100%) and
- 10 ml of chloroform.

The 20 ml HS-vial is sealed gas-tight with a septum. It is then extracted 30 min in an ultrasonic bath at room temperature (or by intense agitation).

The supernatant is removed with a disposable syringe and filtered, by using a syringe PTFE-filter (0.45 µm), into a 2 ml GC-vial. Usually, a clear solution is obtained.

Remarks:

- The amount of added acetic acid shouldn't be changed because a weak acidic pH-value is important. Due to the possibility that some products have an alkaline pH or contain basic functional groups, part of the added acetic acid can be consumed.
  [*Note:* In alkaline or too acidic medium, especially at higher temperatures, a regression of silicone cycles from the silicones contained in the samples is possible.]
- In the case of products containing water, the addition of sodium sulfate can lead to (significant) caking. This can be avoided by using a mixture of sodium sulfate and magnesium sulfate (1:1) as desiccant.
- If the solution does not become clear, reducing the sample weight to, for example, 0.5 g and the desiccant, for example, 4 g can be helpful (especially if only sodium sulfate is used as the desiccant), as the two phases separate more easily, and the solution will clear more quickly.

4. Measurement (GC/MS or GC-FID)

GC parameters		
Oven:	Initial temperature:	40 °C / 2 min
	Rate:	10 °C / min
	Final temperature:	280 °C / 15 min
Injector:	Mode:	Split
	Split ratio:	1:25
	Flow:	1.0 ml / min of helium
	Injection temperature:	120 °C [2]
Column:		Varian CP8771 CP-SIL8 CB
	Length:	30.0 m
	Diameter:	250 µm
	Film thickness:	1.0 µm
Detector:	MSD (SIM mode: M: 281) or (FID)	

Remarks:

- Avoid contamination with silicones, e.g., via seals, lubricants, care and cleaning products or cosmetics (soaps, hand- and face creams) as well as pre-loaded columns.
- Water in the test sample must be completely removed, otherwise the measured values will be falsified (risk of too high measured values).
- Change injection tubes for each measurement to avoid contamination.
- It is important to measure a blind control, too.
- It is additionally recommended to measure a blank sample after each analyzed sample sequence to check whether carry-over has occurred.
- By using linear D5 (dodecamethylpentasiloxane) as an internal standard during the measurement, the reproducibility of the measurement can be improved (see also note under point 6 "Validation").
- Simultaneous determination of octamethyltrisiloxane and hexamethylcyclotrisiloxane (lin. and cycl. D3 silicones) increases the certainty of the determination, since D3 silicones are rather rarely present. Therefore, D3 silicones are indicators that something has gone wrong in the measurement.
- GC method carries a risk of silicone cycles regression, so the injection temperature should not exceed 120 °C.

Potential problems:

- Residual water
- Emulsifiers in the samples
- Sample matrix

[2] The application of higher injector temperatures was tested, but showed no differences compared to the temperature 120 °C even with the higher cycles D5 and D6, but the risk of silicone polymers splitting back to D4.

5. Evaluation:

External standard method using linear regression (5-point calibration)

6. Validation:

5-point calibration:

Stock solution: Place 10 mg of D4-Siloxane in a 10 ml volumetric flask and fill-up to the mark with chloroform (= 1 mg/ml D4).

Calibration solution 1: Pipette 1 ml of stock solution into a 10 ml volumetric flask and fill up to the mark with chloroform (= 100 µg/ml D4).

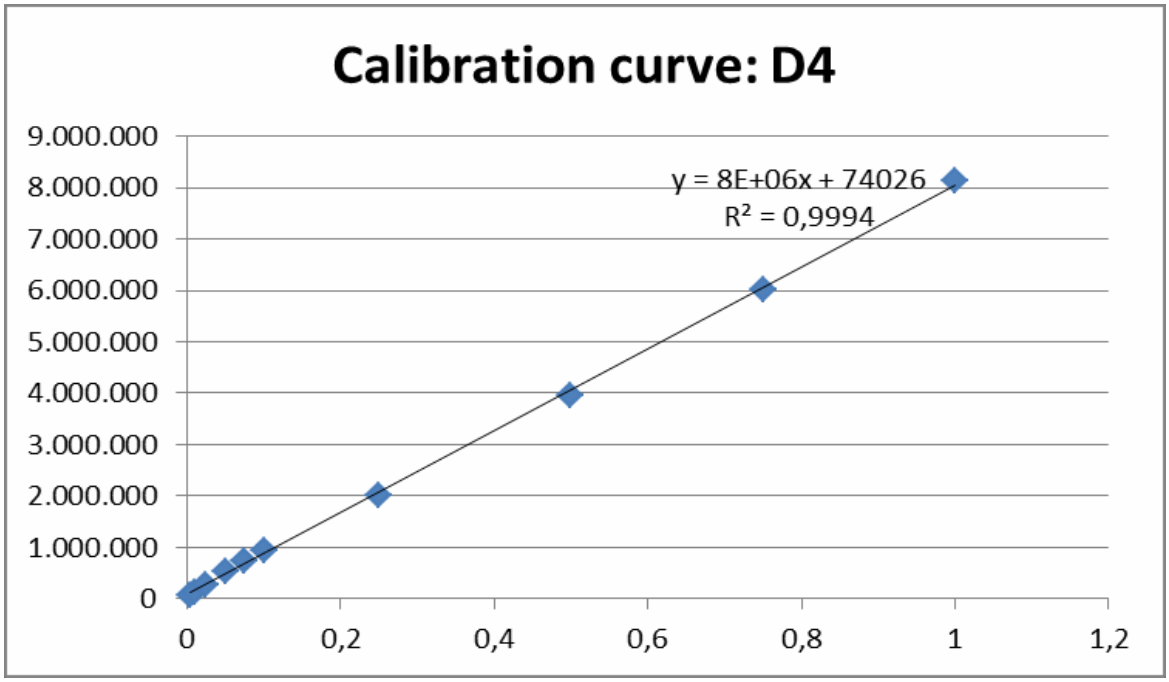
Calibration solution 2: Pipette 0.5 ml of stock solution into a 10 ml volumetric flask and fill up to the mark with chloroform (= 50 µg/ml D4).

Calibration solution 3: Pipette 0.1 ml of stock solution into a 10 ml volumetric flask and fill up to the mark with chloroform (= 10 µg/ml D4).

Calibration solution 4: Pipette 0.05 ml of stock solution into a 10 ml volumetric flask and fill up to the mark with chloroform (= 5 µg/ml D4).

Calibration solution 5: Pipette 1 ml of calibration solution 3 into a 10 ml volumetric flask and fill up to the mark with chloroform (= 1 µg/ml D4).

Reference calibration graph in validation



LoQ: 1 µg/ml D4

Note:

Calibration with two calibration curves 1.) Mixture D4/D6 as well as 2.) D5 (each with internal standard linear D5) improves the result compared to only one calibration curve with a mixture D4/D5/D6 (reason: the substances D4, D5 and D6 are never pure, i.e. always contain the other two cycles as impurities). For better sensitivity at the MSD, the following masses D4=281Da / D5=267Da / D6=341Da / L5=281Da (ISTD) can be used

7. Remarks

Limitation of the method:

- In the case of highly viscous and cross-linked silicones, the measurement of residual cycles can be difficult, as these compounds may not be (completely) dissolved.

- In the case of quaternary aminosiloxanes in pure form, the reproduction of Si cycles occurs due to autocatalytic processes. The replication takes place (partly very) slowly, but goes up to the equilibration, i.e. up to residual contents of residual cycles in the percentage range. Therefore, a measurement of these silicone polymers before equilibrium is reached, e.g. directly after production and distillation, is not meaningful.

- If quaternary aminosiloxanes are brought into solution directly after synthesis and distillation for the preparation of mirco- or macroemulsions, especially in aqueous solution, no reversion of the Si cycles takes place.

- In the case of pure aminosiloxanes, similar but usually much weaker effects can occur. Here, too, there is no regression of Si cycles in solution.

- The same applies to siloxanes for which the catalyst used cannot be deactivated (i.e. destroyed or neutralized) or separated after polymer synthesis. In these cases, too, regression of Si cycles can occur over the duration of storage.

8. applicable documents