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Solar thermal electric plants –
Part 1-6: Silicone-based heat transfer fluids for use in line-focus concentrated solar power applications

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Part 1-6: Silicone-based heat transfer fluids for use in line-focus concentrated solar power applications

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Full information on the voting for its approval can be found in the report on voting indicated in the above table.

The language used for the development of this International Standard is English.

This document was drafted in accordance with ISO/IEC Directives, Part 2, and developed in accordance with ISO/IEC Directives, Part 1 and ISO/IEC Directives, IEC Supplement, available at www.iec.ch/members_experts/refdocs. The main document types developed by IEC are described in greater detail at http://www.iec.ch/standardsdev/publications.

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SOLAR THERMAL ELECTRIC PLANTS –

Part 1-6: Silicone-based heat transfer fluids for use in line-focus concentrated solar power applications

1 Scope

This part of IEC 62862 specifies the technical requirements (safety and physical parameters), test methods, inspection rules and intervals, sampling, judgment, marking, labelling and accompanying documents, packaging, transportation and storage, recycling and disposal of silicone-based heat transfer fluids (SiHTF) for use in line-focusing solar thermal power plants.

The application of polydimethylsiloxane-based heat transfer fluids for this type of installation is covered in this document. Owing to their chemical nature and composition, the introduction of new test methods to determine the applicability and the thermal stability of SiHTF is included in this document.

2 Normative references

The following documents are referred to in the text in such a way that some or all of their content constitutes requirements of this document. For dated references, only the edition cited applies. For undated references, the latest edition of the referenced document (including any amendments) applies.

IEC TS 62862-1-1, *Solar thermal electric plants – Part 1-1: Terminology*

ISO 2049, *Petroleum products – Determination of colour (ASTM scale)*

ISO 2160, *Petroleum products – Corrosiveness to copper – Copper strip test*

ISO 2719, *Determination of flash point – Pensky-Martens closed cup method*

ISO 3016, *Petroleum and related products from natural or synthetic sources – Determination of pour point*

ISO 3104, *Petroleum products – Transparent and opaque liquids – Determination of kinematic viscosity and calculation of dynamic viscosity*

ISO 3405, *Petroleum and related products from natural or synthetic sources – Determination of distillation characteristics at atmospheric pressure*

ISO 3675, *Crude petroleum and liquid petroleum products – Laboratory determination of density – Hydrometer method*

ISO 6618, *Petroleum products and lubricants – Determination of acid or base number – Colour-indicator titration method*

ISO 11885, *Water quality – Determination of selected elements by inductively coupled plasma optical emission spectrometry (ICP-OES)*

ISO 12185, *Crude petroleum and petroleum products – Determination of density – Oscillating U-tube method*

ISO 12937, *Petroleum products – Determination of water – Coulometric Karl Fischer titration method*

ISO 15597, *Petroleum and related products – Determination of chlorine and bromine content – Wavelength-dispersive X-ray fluorescence spectrometry*

ISO 20846, *Petroleum products – Determination of sulfur content of automotive fuels – Ultraviolet fluorescence method*

UNE 206015, *Heat transfer fluids for solar thermal power plants with parabolic trough collector technology. Requirements and tests*

DIN 4754-1, *Wärmeübertragungsanlagen mit organischen Wärmeträgern – Teil 1: Sicherheitstechnische Anforderungen, Prüfung* (in German) [*Heat transfer installations working with organic heat transfer fluids – Part 1: Safety requirements, test*]

DIN 51529, *Prüfung von Mineralölen und verwandten Erzeugnissen – Prüfung und Beurteilung gebrauchter Wärmeträgermedien* (in German) [*Testing of mineral oils and related products –* Testing and evaluation of used heat transfer fluids]

DIN 51794-2003-05, *Prüfung von Mineralölkohlenwasserstoffen – Bestimmung der Zündtemperatur* (in German) [Testing of mineral oil hydrocarbons – Determination of ignition temperature]

3 Terms and definitions

For the purposes of this document, the terms and definitions given in IEC TS 62862-1-1 and the following apply.

ISO and IEC maintain terminological databases for use in standardization at the following addresses:

- IEC Electropedia: available at http://www.electropedia.org/
- ISO Online browsing platform: available at http://www.iso.org/obp

3.1 General definitions

3.1.1
heat transfer fluid
HTF
substances in the liquid or gaseous phase that are used for heat transfer

3.1.2
unused heat transfer fluid
heat transfer fluid which has not been introduced into the heat transfer system, e.g. the solar field

3.1.3
heat transfer fluid in use
heat transfer fluid which has been introduced into the heat transfer system at least once

3.1.4
heat transfer fluid at operating conditions
heat transfer fluid which is operated at the specified working temperature, after reaching a chemical equilibrium state

3.1.5
equilibration
process of reaching equilibrium composition under specific temperature and pressure parameters

Note 1 to entry: In a chemical reaction, equilibrium is the state in which both the reactants and products are present in concentrations which have no further tendency to change with time, so that there is no observable change in the properties of the system. Typically, silicone-based heat transfer fluids at a given temperature and pressure experience changes of their physical properties until a chemical equilibrium is established. Afterwards, the physical properties and chemical composition of the fluid remain stable.

3.1.6
maximum working temperature
maximum bulk temperature of the heat transfer fluid permitted at any location in the heat transfer fluid system

3.1.7
maximum bulk temperature
highest average temperature of the heat transfer fluid in a specified section of the installation

Note 1 to entry: The location of the section of the installation with the maximum bulk temperature is usually directly after the exit of the hot collector outlet or at the exit of a fluid heater.

3.1.8
film temperature
temperature at the contact between heat transfer fluid and heating surface of the solar receiver, heater, or other components

3.1.9
zeotropic mixture
complex mixture with liquid components that have different boiling points

Note 1 to entry: Individual substances in the mixture do not evaporate or condense at the same temperature as a pure substance.

3.2 Relevant physical and chemical properties of heat transfer fluids

3.2.1
appearance
<of heat transfer fluid> parameter describing the purity of a heat transfer fluid, referring to the absence or presence of turbidity, emulsion, particles or visible water in the heat transfer fluid

Note 1 to entry: The appearance and color of a heat transfer fluid can be useful for a comparative assessment. A change in color, or the appearance of particles, may indicate degradation or contamination of the liquid.

3.2.2
composition
<of heat transfer fluid> information on the chemical identity of the medium or its individual components

Note 1 to entry: For complex mixtures information on the chemical identity can be also the chemical family instead of individual compounds. The physical and chemicals properties of the HTF are very relevant for concentrated solar power (CSP) application. These properties and the health, safety and environment (HSE) classification is determined by the type of chemistry of the HTF. The chemical composition of siloxanes can be determined by gas chromatography–mass spectrometry (GC-MS).

3.2.3
water content

<of heat transfer fluid> amount of water in the heat transfer fluid, given on a mass (gravimetric) basis

Note 1 to entry: High water content leads to higher vapor pressure. It may also impact the corrosivity and other parameters like aging rate of an HTF and hydrogen formation rate and thus the concentration of particles or degradation products. Concerning SiHTFs, high amounts of water may also lead to water-induced degradation reactions. In consequence fluid viscosity may increase significantly faster and shorten shelf-life. The occurrence of water in the heat transfer fluid is usually due to a defective point in the heat exchange system.

3.2.4
chlorine content

<of heat transfer fluid> amount of chlorine in the heat transfer fluid, given on a mass (gravimetric) basis

Note 1 to entry: Corrosiveness and the degradation rate of the HTF may increase with increasing chlorine concentration, thus the chlorine content of the heat transfer medium shall be known.

3.2.5
sulphur content

<of heat transfer fluid> amount of sulphur in the heat transfer fluid, given on a mass (gravimetric) basis

Note 1 to entry: The corrosiveness and the degradation rate of the HTF may increase with increasing sulphur concentration, thus the sulphur content of the heat transfer medium shall be known.

3.2.6
acid number
neutralization number

<for water soluble acids> required basic amount (shown in milligrams of potassium hydroxide) to neutralize the acid content in one gram of the heat transfer fluid sample (mg KOH/g HTF)

3.2.7
copper corrosion

corrosion of materials made of copper or copper alloys when exposed to the HTF itself or any other compounds in the HTF

Note 1 to entry: The relative degree of corrosiveness can be determined by the copper strip test.

3.2.8
flash point

minimum temperature at which a flame on the surface of a heat transfer fluid triggers the ignition of the liquid's vapor (°C)

Note 1 to entry: The flash point determines the flammability classification of the liquid and thus the transport regulations (hazardous goods), as well as measures for occupational and plant safety. During operation of a CSP plant the fluid is typically operated significantly above the flash point temperature. Accordingly, the system is designed for it, and all surfaces of the fluid are covered with inert gas (nitrogen).

3.2.9
auto-ignition temperature

temperature at which a heat transfer fluid self-ignites in the presence of air but in the absence of flames or sparks that could trigger combustion (°C)

Note 1 to entry: The auto-ignition temperature of a medium is required to specify equipment suitable for the use in potentially explosive atmospheres (areas prone to leakages). The surface temperatures shall either be limited to a safe value below the auto-ignition temperature, or other measures to prevent fire in accordance with the results of a hazard analysis have to be taken.

3.2.10
heat of combustion

amount of energy released when a unit of mass of a heat transfer fluid is burned in the presence of oxygen (J/kg)

3.2.11
viscosity

resistance of a liquid to flow under the action of gravity, which arises from the internal friction of a fluid

Note 1 to entry: The kinematic viscosity is related to the dynamic viscosity by dividing with the density. The dynamic viscosity is usually given in Pa·s, while the value of the kinetic viscosity is given in mm^2/s. This is a temperature-dependent physical quantity. The kinematic viscosity is a relevant parameter for the evaluation of the flowing and pumping behavior of the HTF. It influences the pressure losses. Aging and oxidation of the fluid tend to change the fluid viscosity.

3.2.12
density

mass per unit volume (kg/m^3); a temperature- and pressure-dependent physical quantity

3.2.13
pour point

temperature below which the liquid loses its flow characteristics

Note 1 to entry: The pour point is the parameter to define the lowest operating temperature. If the pour point of the HTF is above ambient temperature, special technical precautions for HTF heating shall be taken, especially during commissioning and longer standstills of the plant or parts of the plant.

3.2.14
cloud point

<in liquids> temperature below which a transparent solution undergoes either a liquid-liquid phase separation to form an emulsion or a liquid-solid phase transition to form either a stable solution or a suspension that settles a precipitate (cloudy appearance)

Note 1 to entry: The presence of solidified particles thickens the fluid and may clog filters in the system. The solidified particles may also accumulate on cold surfaces.

3.2.15
normal boiling point

temperature at which the vapor pressure of the liquid (azeotropic mixtures) equals the atmospheric pressure at sea level

Note 1 to entry: The boiling temperature at ambient pressure influences in particular the handling of the heat transfer medium during commissioning.

3.2.16
boiling range

temperature range involved in the distillation of zeotropic mixtures, from the start to the temperature when the component with the highest boiling point evaporates

Note 1 to entry: During operation, a fluid pressure above the vapor pressure of the heat transfer medium at any point of the system is required.

3.2.17
heat of evaporation

amount of energy (heat) that has to be absorbed by a unit of mass of a heat transfer fluid in order to evaporate at a given temperature and pressure (J/kg)

3.2.18
maximum film temperature

maximum permitted temperature in the heat transfer system at the contact between the heat transfer fluid and the heating surface of the solar receiver, heater, or other components

3.2.19
insoluble product
content of inorganic particles and insoluble degradation products, e.g., solid waste materials like coke in a heat transfer fluid sample

Note 1 to entry: This parameter analyses the possible change in the composition of the heat transfer fluid due to degradation and/or contamination.

Note 2 to entry: Insoluble products can be defined by lack of solubility of solid compounds in specific solvents like e.g., acetone, toluene or pentane. Another definition is lack of solubility of solid compounds in the HTF at a specific temperature.

Note 3 to entry: Insoluble compounds can be caused by degradation products of the HTF, by corrosion products of steel or by contamination with dirt, e.g., from welding processes. Hence, the kind of insoluble products may indicate contamination by dirt, corrosion products e.g., due to enhanced humidity, or significant thermal stress of the HTF. Insoluble products may decrease heat transfer on surfaces. They may also cause clogging or blockage of pipelines e.g., in cases of prolonged overheating or wear and clogging of seals and valves.

3.2.20
metal content
amount of metals in the heat transfer fluid

Note 1 to entry: The metal content is relevant because high contents e.g. of chromium can generate environmental and health risks. Furthermore, heat transfer oils could contain traces of metals, either caused by corrosion processes in case of high-water levels in the HTF system, abrasion in the production process or by ongoing operation in heat transfer systems. Some metals could have a catalytic effect on the degradation of the HTF itself or could clog filters.

3.2.21
heat conductivity
ability of a heat transfer fluid to transfer heat (W/(m K))

Note 1 to entry: The thermal conductivity affects the Prandtl number which, in turn, affects the heat transfer coefficient. The Prandtl number describes the heat transport by momentum exchange in relation to the heat transport by heat conduction within a fluid. This means that a high thermal conductivity increases the heat transport (at the same flow velocity) and ensures a low temperature gradient in the laminar boundary layer (from the core temperature to the film temperature of the flow).

Note 2 to entry: Heat conductivity is a temperature-dependent quantity.

3.2.22
heat capacity
energy required to increase the temperature of a specific amount of heat transfer fluid (J/(gK))

Note 1 to entry: Heat capacity is a thermodynamic property of the liquid that is related to the energy transport from the solar field. The higher the value, the more energy the liquid takes up on the increase in temperature.

Note 2 to entry: Heat capacity is a temperature-dependent variable.

3.2.23
vapor pressure
pressure exerted by the gaseous phase of a heat transfer fluid that is in equilibrium with the liquid phase at a given temperature (Pa)

Note 1 to entry: The vapor pressure of the HTF together with the pressure losses (and additional safety measures) determines the design pressure of the CSP subsystems. High vapor pressures lead to increased plant costs. If the medium in its area of application has a vapor pressure above the ambient pressure, pressure vessels are required which cause considerable costs.

3.2.24
thermal degradation
degradation where damaging chemical changes on a molecular level take place at elevated temperatures, without the simultaneous involvement of other compounds such as oxygen

Note 1 to entry: Even in the absence of air, molecular compounds (like polydimethylsiloxanes) will begin to degrade if the temperature is high enough.

3.2.25
thermal stability
resistance of a heat transfer fluid to thermal degradation within a temperature range for which it is specified

Note 1 to entry: The thermal stability of an HTF typically limits and thus determines the maximum working temperature of parabolic trough power plants. This value is also used to estimate the life span and exchange rate (if needed) of the heat transfer fluid at operating conditions.

4 Classification of heat transfer fluids

4.1 General

For the purposes of this document, the heat transfer fluids are classified as follows in 4.2 to 4.6.

4.2 Mineral oil fluids

Oil obtained from crude oil by refining processes.

4.3 Synthetic fluids

Liquid obtained mainly from the synthesis of various organic compounds.

4.4 Synthetic heat transfer fluids based on polydimethylsiloxanes (silicone, SiHTF)

Liquid composed of polydimethylsiloxanes (CAS No. 63148-62-9, $CH_3[Si(CH_3)_2O]_nSi(CH_3)_3$); depending on the composition stable above 400 °C.

4.5 Organic synthetic heat transfer fluids based on biphenyl / diphenyl oxide (BP/DPO)

Liquid from the eutectic mixture of biphenyl (CAS No. 92-52-4, $C_{12}H_{10}$) and diphenyl oxide (CAS No. 101-84-8, $C_{12}H_{10}O$).

4.6 Molten salt

Inorganic salt in liquid state usually composed of mixtures of alkali nitrates, carbonates, chlorides, etc.

5 Specified fluid properties and test methods

5.1 General

The tests listed in this Clause 5 are considered to determine whether the fluid is suitable for use in solar thermal applications. If the fluid is already in use the test items should ensure that it can still be safely operated within its design limits.

5.2 List of technical requirements and evaluation of the quality of unused heat transfer fluids

Table 1 – Properties and test methods for unused heat transfer fluids

Property	Test method	Alternative test method	Reference value
Appearance	ISO 2049		Transparent without suspended solids
Composition	Identity of the component class GC-MS		Polydimethylsiloxane (material safety data sheet)
Water content	ISO 12937	DIN 51777 [1] [1] SH/T0246-1992 [2]	< 100 ppm [3]
Chlorine content	ISO 15597	DIN 51408-2 [4]	< 10 ppm (UNE 206015)
Sulphur content	ISO 20846	SH/T0689-2000 [5] ISO 20884 [6] ISO 14596 [7]	< 10 ppm (UNE 206015)
Acid number (water soluble acids)	ISO 6618	DIN 51558-2 [8]	< 0,2 mg KOH/g (UNE 206015)
Copper corrosion	ISO 2160		< 1 a (UNE 206015)
Flash point (closed cup)[a]	ISO 2719	GB/T261-2008 [9]	110 °C, (UNE 206015)
Auto-ignition temperature	DIN 51794-2003-05	ASTM E659-15 [10] SH/T0642-1997 [11]	In °C, no general reference value available
Heat of combustion		DIN 51900-1 [12]	In kJ/kg, no general reference value available
Kinematic viscosity, at 0 °C Kinematic viscosity, at 25 °C Kinematic viscosity, at 100 °C	ISO 3104	DIN 53019 [13] GB/T265-1988 [14]	In mm/s^2, no general reference value available
Density, at 25 °C	ISO 3675 ISO 12185	ASTM D1298 [15] ASTM D4052-22 [16] DIN 51757 [17] SH/T0604-2000 [18]	In kg/m^3, no general reference value available
Freeze point, pour point, cloud point	ISO 3016	GB/T3535-2006 [19]	In °C, no general reference value available
Normal boiling point/boiling range	ISO 3405		In °C, no general reference value available
Normal heat of evaporation[b]	No method		In kJ/kg, no general reference value available
Maximum film temperature recommended	No method		In °C, product data sheet, no general reference value available
Maximum working temperature	No method		In °C, product data sheet, no general reference value available

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[1] Numbers in square brackets refer to the Bibliography.

[*] The term ppm (parts per million) is commonly used for the concentration 10^{-6}.

[a] The flash point in the closed cup method is conducted inside a closed vessel which is not open to the outside atmosphere. The lid is sealed, and the ignition source is introduced into the vessel itself, allowing for a closer approximation to real-life conditions (such as those found inside an HTF tank).

[b] There is no standard method available for zeotropic mixtures, thus the value shall be estimated with sufficient safety margin.

Standard test methods are given in the test method column. The alternative test method may be followed. Reference values are for the unused liquid. The deviations from these reference values shall be agreed between the customer and the supplier.

5.3 List of additional fluid properties and test methods for silicone-based heat transfer fluids for general layout at operating conditions

All parameters mentioned in Table 2 shall be specified for the heat transfer fluid at operating conditions due to the equilibration of the polydimethylsiloxane-based HTF upon heating above 200 °C (see 3.1.4 and 3.1.5).

Therefore, the properties in Table 2 required for the design of heat transfer systems shall be specified at operating conditions, together with the intended temperature range, and indicating the applied test method.

Table 2 – Additional fluid properties at specified operating conditions

Property	Unit
Kinematic or dynamic viscosity	mm^2/s or mPa s
Density	kg/m^3
Heat conductivity	W/(m·K)
Isobaric heat capacity	kJ/(kg·K)
Vapor pressure	kPa
Solubility of nitrogen	mmol/kg
Formation of hydrogen	µmol/(kg·h)
Formation of methane	µmol/(kg·h)
At the time of publication, no standard test methods for the parameters at operating conditions given in this Table 2 are available. The supplier or manufacturer shall therefore specify the test conditions.	

5.4 List of fluid properties and test methods for heat transfer fluids in use

The further usability of the heat transfer fluid results from the tests listed in Table 3, if necessary, from the additional tests listed in Table 4 in connection with the limit values given by the fluid manufacturer or supplier. The test items in Table 4 are focused on decomposition products and plant-related impurities. According to DIN 51529, compliance with the limit values recommended by the manufacturer is crucial for assessing the reusability of the system filling. The definition of the limit values for the assessment of further usability is based on the general experience of the manufacturers and suppliers of the heat transfer fluid. If there are special circumstances and with regard to system-specific features, an overall assessment can only be made in conjunction with the system operator.

Table 3 –Test methods for heat transfer fluids in use (basic program)

Property	Test method	Alternative test method
Appearance	ISO 2049	
Water content	ISO 12937	DIN 51777 SH/T0246-1992
Acid number (water soluble acids)	ISO 6618	DIN 51558-2
Flash point (closed cup)	ISO 2719	GB/T 261-2008
Kinematic viscosity (25 °C)	ISO 3104	DIN 53019 GB/T265-1988
Standard test methods are given in the test method column. The alternative test method may be followed.		

Table 4 – Test methods for heat transfer fluids in use (additional program)

Property	Test method	Alternative test method
Insoluble products	ASTM D 893 [20]	
Metal content[a]	ISO 11885[b]	
Chlorine content[c]	ISO 15597	
Sulphur content[d]	ISO 20846	SH/T0689-2000
Thermal degradation	T-group method (Annex A)	
Gas concentration (H_2, Methane)	Evaluation of cylinder samples (6.3)	
Standard test methods are given in the test method column. The alternative test method may be followed.		

[a] Metals can indicate impurities from the system.

[b] Metal content shall be transferred into water-soluble components e.g. by closed microwave acid digestion (HF/HNO_3) with subsequent ICP-OES or ICP-MS measurement. [21]

[c] Chlorine can indicate impurities from the system.

[d] Sulphur can indicate impurities from the system.

6 Inspection interval and sampling

6.1 Inspection interval

Heat transfer fluids in an operating plant shall be checked for their serviceability once a year or on demand in accordance with DIN 4754-1. Therefore, the heat transfer fluids in use shall be sampled and inspected at least once a year in accordance with all items listed in Table 3. In any of the following cases of demand, sampling inspection shall be conducted (safety recommendations, instructions and fluid handling recommendations are given in Annex B):

- After the filling process but before heating up the system for the first time.
- After the initial start-up.
- Three months after the initial start-up period.
- Irregularities of the process which could harm the heat transfer fluid e.g. overheating/contamination.
- Change of the operating mode.
- Three months after a change-over from a different heat transfer fluid.

6.2 HTF sampling

Sampling of heat transfer fluids shall meet the following requirements:

- The sample taken shall be a uniform sample representing the quality status of the heat transfer fluids currently in use in the system, i.e., it should preferably be taken from the main circulating line of the system, e.g., from the cold side of the loop, not from the expansion vessel (risk of non-representative sample). Occasionally, additional samples may have to be taken from other parts of the system if specific problems exist.
- The heat transfer fluid should be sampled while cold below its flash point (<< 50 °C). A hermetic container as shown in Figure 1 shall be used to prevent the escape of low boilers and gases which otherwise would be lost from the sample.
- Before sampling, the sampling container should be thoroughly flushed with inert gas.

Sampling bottles of the following type which comply with UNE 206015 standard (Heat transfer fluids for solar thermal power plants with parabolic trough collector technology. Requirements and tests) shall be used:

- An impermeable, clean and dry container shall be used for storing the heat transfer fluid from sampling to enable laboratory analysis.
- The container shall be made of a material that is compatible with the heat transfer fluid and suitable for its transport in order to preserve the chemical properties of the sample during this entire period. The materials compatible with the HTF are preferably pure aluminum (material AL 99.5) or borosilicate glass.
- With tamper-evident screw cap made of PP with aluminum inner seal.
- With UN approval (1B1/X/250).
- Packaging group I (X).

Figure 1 – Example of an aluminum bottle for sampling (new)

6.3 Gas-sampling

For gas analysis representative samples containing HTF and gas in the same relative ratio as in the fluid system may be obtained by collecting samples with steel cylinders that are equipped with valves.

- Components of cylinders and valves shall be chosen that withstand the temperature and pressure of the heat transfer system. For sufficient gas tightness compression fittings or welded connections should be used between valves and cylinders (Figure 2).
- 300 ml cylinders and connection sizes between 6 mm and 10 mm (1/4" / 3/8") should be used.

- For collecting representative samples, the cylinders should be connected in vertical position between the high-pressure inlet and the lower pressure outlet of the solar field via compression fittings at connection points equipped with valves (e.g. drain valves). Sampling points should be connected to the cylinder with 0,953 cm (3/8 inch) tubing with total length less than 6 m. The high pressure side shall be connected to the bottom valve and the low-pressure side to the top valve of the cylinder.
- Air should be removed from the cylinder by flushing with nitrogen via extra connections while the cylinder is mounted ready for collecting the sample to avoid oxygen contamination of the heat transfer system. Nitrogen quality should correspond at least to the one used as blanket gas in the heat transfer system. Instead of flushing with nitrogen the cylinder may be pressurized with 10 bar nitrogen which is then decompressed at the outlet of the cylinder to atmosphere. This should be performed at least three times to remove oxygen.
- The cylinder should be filled with the HTF sample by completely opening all valves required to enable passage from the inlet to the outlet. HTF flow through the cylinder should be maintained for at least 2 min to ensure that any gas bubbles are flushed out of the device and that it is filled only with the HTF sample with dissolved gas. Sufficient quality of the sampling process should be checked with the sample mass obtained by weighing the empty and the filled cylinder. The sample mass should correspond to the cylinder volume times sample density at the temperature of the sampling process.
- After the cylinder is filled, the outlet valve of the cylinder shall be closed before closing the inlet valve directly afterwards.
- The closed cylinder is disconnected from the system after cooling down and after closing all other included valves, including those to the heat transfer system.
- The sample should be sent to a specialized laboratory for analysis in a transport container that protects the cylinder and valves from damage. After ensuring that the valves are firmly closed and that the sample is cool, the valve' handles shall be disconnected.
- Evaluation of hydrogen or any other gas content shall be performed according to the literature method described in [22].

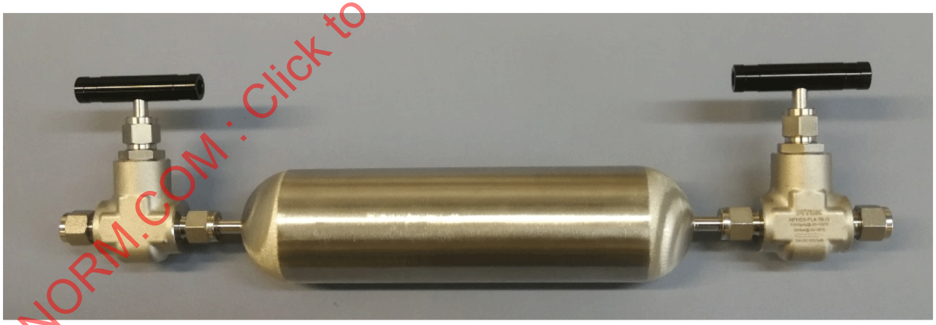

Figure 2 – Example of a cylinder mounted with two valves (before use) e.g. for sampling at 425 °C and 20 bar

6.4 Labeling of the samples

After sampling, the sampling bottle/cylinder shall be tightly closed and labelled. The cylinder shall be marked with date and serial number (e.g., 2023-01-31 0045). An accompanying one-page form shall be added including said date, serial number and following data:

1) Customer data
   a) Company
   b) Contact person
   c) Address
   d) Phone
   e) Email

2) Information about the facility
    a) Address of the operator company, Location
    b) Application
    c) Date of commissioning
    d) Sampling location
    e) Volume used in the operating system
    f) Use of inert gas (nitrogen or argon)
3) Information about the sample
    a) Sample identification
    b) Trade name of the heat transfer fluid
    c) Type of liquid, classification
    d) Date and time of sampling
    e) Weight (or volume) of the liquid
    f) Person who takes the sample
    g) Reasons for the analysis (routine or otherwise)
    h) Hours of operation / Age of the heat carrier
    i) Date of the last processing of the liquid (filling, filtering, etc.)
    j) Liquid temperature at the entrance to the solar field
    k) Liquid temperature at the exit of the solar field
    l) Change in operating conditions (pressure, temperature, mass flow)

7 Reporting

The progress of the liquid analyses, the trend graphs of the most important parameters and the acceptable and/or no longer acceptable limit values of the various parameters described in Clause 5 shall be given in the report sheet.

In all cases, the results report sheet should contain the following information:

1) Customer data
    a) Company
    b) Contact person
    c) Address
    d) Phone
    e) Email
2) Information about the facility
    a) Address of the operator company, Location
    b) Application
    c) Date of commissioning
    d) Sampling location
    e) Fluid volume in the heat transfer system
    f) Use of inert gas (nitrogen or argon)

3) Information about the sample
    a) Sample identification
    b) Trade name of the heat transfer fluid
    c) Type of liquid, classification
    d) Date of sampling
    e) Weight (or volume) of the liquid
    f) Person who takes the sample
    g) Reasons for the analysis (routine or otherwise)
    h) Hours of operation / Age of the heat carrier
    i) Date of the last processing of the liquid (filling, filtering, etc.)
    j) Date of receipt
    k) Date of analysis
4) Reference to last sample diagnosis
5) Results (and respective test method)
    a) Basic program
        i) Appearance
        ii) Water (mg/kg or ppm)
        iii) Acid number (water soluble acids) (in mg KOH/g)
        iv) Flash point (closed cup) in °C
        v) Kinematic viscosity (25 °C) in mm^2/s
    b) Additional program
        i) Insoluble products
        ii) Metal content in ppm
        iii) Chlorine content in ppm
        iv) Sulphur content in ppm
        v) Degradation

8 Marking, labelling and accompanied documents

The mark and label of the product shall include product name, trademark, model, batch number, net weight, manufacturer's name and address, etc.

The following accompanying documents shall be provided on delivery of each batch of products:

- Certificate of analysis (CoA);
- Technical data sheet;
- Material safety data sheet.

9 Mixing

Heat transfer fluids with different chemical and physical properties shall not be mixed into the same system.

10 Recycling and disposal

For silicone-based heat transfer fluids in use which are intended for recycling, distillation and filtration may be used to remove contaminants. With these measures the quality of the heat transfer fluids can be improved to a certain extent. Hence, the heat transfer fluid may be returned to the original system for further use. This is permitted if the parameters according to Table 1 under normal operating conditions are met.

In the process of recycling, no other chemical additives should be added to change the physical properties.

Recycling of silicone based HTF is generally possible and shall be evaluated by the corresponding manufacturer or supplier. If recycling is not an option, the disposal of the HTF can be subject to regulatory requirements.

11 Replacement and disuse

The need for partial or complete replacement of the heat transfer fluid shall be evaluated and determined by the customer and supplier / manufacturer together as it depends on the working conditions and the facility the fluid is used in.

The replaced heat transfer fluid is recycled or disposed of taking into account that local laws and regulations can apply.

Annex A
(informative)

Determination of the degree of thermal degradation of polydimethylsiloxane-based heat transfer fluids

A.1 Overview

This test procedure describes how to determine the degradation level of polydimethylsiloxane-based heat transfer fluids. This test procedure is not applicable to other synthetic heat transfer fluids.

Under the laboratory conditions described in this analytical procedure, this method gives information about the effect of heat on SiHTF as a function of temperature and exposure time. The results provide information about the degree of degradation and the further usability of the SiHTF when they are exposed to given elevated temperatures. This analytical method does not provide information about the stability of the SiHTF in general.

The usability limits (e.g., the maximum amount of T-groups tolerable in the SiHTF) and the typical mean annual T-group growth rate at a specific temperature shall be given by the HTF manufacturer or the supplier.

A.2 Meaning of symbols M, D, T

M = M-units ($Me_3SiO_{1/2}$): monofunctional trimethylsilyloxy group for end-capping

D = D-units ($Me_2SiO_{2/2}$): difunctional dimethylsilyloxy group for chain-building

T = T-units ($MeSiO_{3/2}$): trifunctional branching methylsilyloxy group

A.3 Principle

SiHTF in general are polymeric mixtures of linear siloxanes consisting of M- and D-units. The thermal stability of SiHTF is assessed by determining the number of T-units formed after exposure to elevated temperatures (Figure A.1).

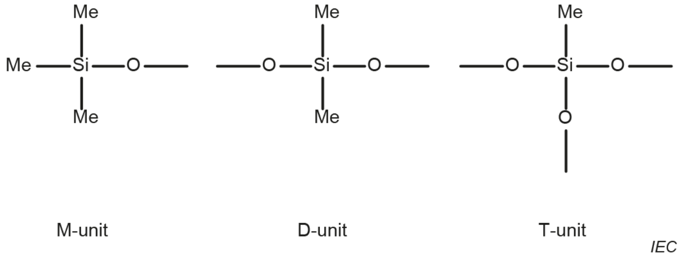

Figure A.1 – Representation of the molecular structure of M-, D-, and T-units in polydimethylsiloxanes (PDMS)

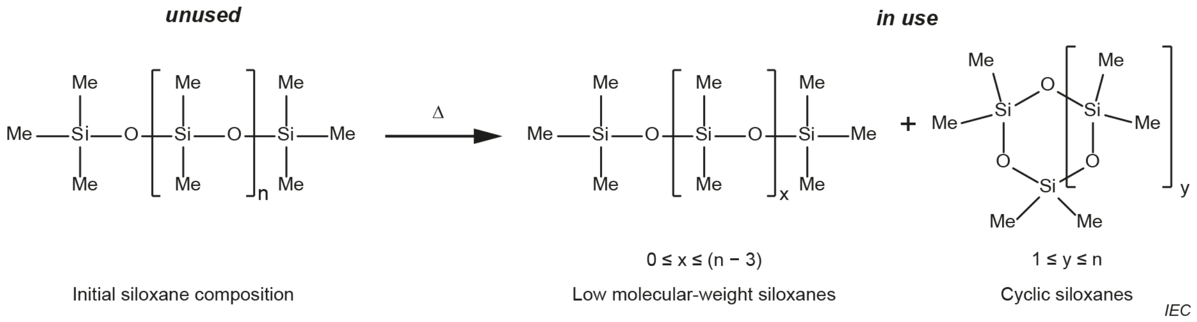

Figure A.2 – Representation of the molecular structure of polydimethylsiloxanes (PDMS, left) and the thermally induced equilibration reaction of linear polydimethylsiloxanes

At temperatures above 250 °C, silicone-based heat transfer fluids (polydimethylsiloxanes) undergo rearrangement reactions (equilibration) of their silicone-oxygen bonds when used as intended (under inert conditions).

The two major relevant processes at high temperatures are:

i) Equilibration: a temperature-dependent equilibrium between linear and cyclic siloxanes (see Figure A.2). Depending on the working temperature the ratio between cyclic and linear components may vary.

ii) Disproportionation: branching T-units and end-capping M-units are formed by a metathesis reaction of two D-units (see Figure A.3). Disproportionation is a slow process and relevant for the determination of the long-term stability. The formation rate of T-groups is also dependent on the temperature, but on a significantly slower time scale than equilibration. Below 400 °C no measurable amount will be formed for long periods of time.

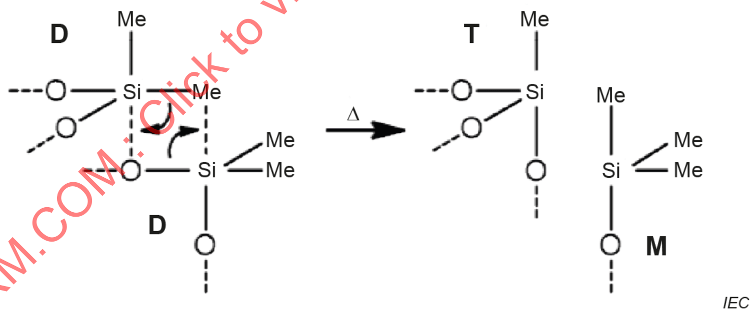

Figure A.3 – Thermally induced disproportionation of D-units in linear polydimethylsiloxanes, into T and M units

The thermal stressing of the polydimethylsiloxane-based heat transfer fluids at temperatures above 250 °C, primarily leads to disproportionation, i.e., the formation of T-groups. With increasing temperature, the disproportionation gains in significance. The thermal formation of these structures only becomes detectable at working temperatures above 400 °C. An increasing number of T-groups may lead to branching points between individual polymer chains. Ultimately, if each polymer chain of a polydisperse mixture has at least two T-units, the system is theoretically completely crosslinked. Crosslinking in general will increase the mean molar mass of the polymer mixture and eventually lead to a long-term increase in viscosity.

It is possible to find a correlation between the number of T-groups and the viscosity increase if the macromolecular properties of a polydimethylsiloxane fluid are known (e.g., mean molar mass, mean molar chain length, general fluid composition). Therefore, the number of T-groups is the most important parameter to determine the current state of the SiHTF and its thermal stability.

To quantify the degree of degradation of the heat transfer fluid the molar amount of T-units can be quantified by ^{29}Si-NMR spectroscopy. To provide a heat transfer fluid with a low viscosity for optimum operating condition the emerging amount of T-groups should be monitored regularly (preferred annually or by individual preference).

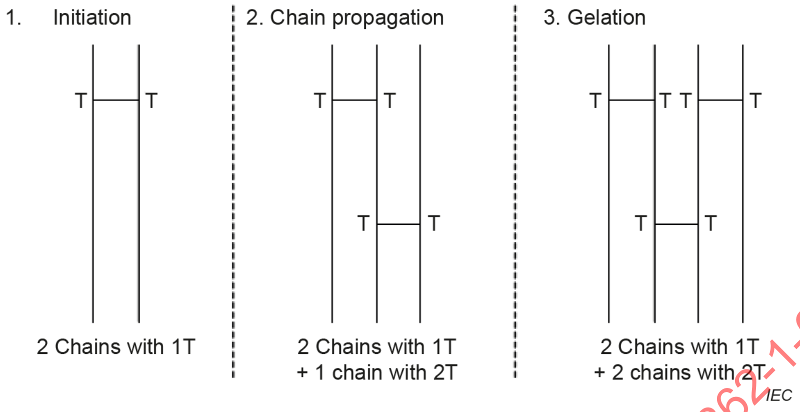

Figure A.4 – Theoretical model for describing the long-term increase in viscosity of polydimethylsiloxane-based fluids by thermal aging

The model shown in Figure A.4 makes it possible to estimate the theoretical gel point of the silicone heat transfer fluids. Hence, the theoretical gel point is a function of the average chain length. Therefore, the amount of T-groups present in the fluid describes the required crosslinking degree with a given chain length.

Concerning the measurement of the thermal stability of silicone fluids, the determination of the T-group amount can be applied:

- Unused silicone fluids contain low values of T-groups (in the lower ppm range < 1 000 ppm).
- During operation above 250 °C, T-groups are continuously formed – the incremental rate thereby increases with higher temperatures. (The formation of these structures only becomes detectable at temperatures above 400 °C.) This will slowly lead to branching of the former separate siloxane molecules. The amount (fraction in percent) of T-units present in the SiHTF is therefore linked with the viscosity of the fluid. In the end, higher amounts of T-units could lead to a viscosity increase.
- The molar amount of T-groups present in the fluid can be determined via ^{29}Si-NMR-spectroscopy.
- The maximum tolerable amount of T-groups depends on the fluid composition (i.e. average chain length) and shall be defined by the fluid manufacturer.

NOTE Metallic or organic impurities, as well as water can induce the formation of T-groups even below temperatures of 400 °C on a significant level (impurities due to maintenance works, HTF exchange).

A.4 Technical equipment

- Commercially available nuclear magnetic resonance (NMR) systems (400 MHz (for ^{1}H and 79,5 MHz for ^{29}Si, or higher field strength if available) equipped with 5 mm barium boric oxide (BBO) probe (or 10 mm BBO probe if available) or comparable systems
- appropriate NMR tubes (borosilicate glass)

- appropriate pulse program for ^{29}Si, e.g. Bruker® ^{29}Si zgig (90 degrees pulse angle) with the following standard parameters:
  - sweep width (sw): 200 ppm
  - time domain size (td): approx. 128 k, minimum 64 k
  - transmitter offset (o1p): −50 ppm
- and the following optimized acquisition parameters:
  - relaxation delay time (d1): e.g. 15 s (adjust d1 to 5 to 7 times of the slowest relaxation signal)
  - number of scans: ns = 3 000

In case of other spectrometer types, the described pulse program can be adjusted according to common procedures (e.g. analysis of T1 and T2 times for optimization of relaxation delay time d1; adaption of "number of scans"). The other parameters of the experiments shall be adjusted as well, if necessary. In any case contact the manufacturer of the technical equipment.

A.5 Safety remarks

Solvents C_6D_6 and toluene are hazardous substances. Benzene is carcinogenic.

A.6 Reagents

If not noted otherwise, commercially available chemicals of the purity grade "p.a. – pro analysis" should be used. For safe handling of the used chemicals check their material safety data sheets provided by their suppliers.

- **Deuterated benzene-d$_6$** (CAS 1076-43-3; 99.6 Atom-% D; water < 0,01 %)
- **Dichloromethane-d$_2$** (CAS 1665-00-5; 99.8 Atom-% D; water < 0,01 %)
- **Chromium(III)acetylacetonate** (CAS 21679-31-2, purity: > 98,0 %)
- **Tetramethylsilane** (TMS or $SiMe_4$; CAS: 75-76-3; purity: > 99,0 %) as common internal standard for ^{29}Si NMR with a chemical shift of δ = 0,0 ppm for spectra calibration.
- **Methyl-tris(trimethylsiloxy)silane** (TM_3; CAS: 17928-28-8; purity: > 99,0 %) is a monodisperse siloxane with a M:T-ratio of 3:1 and can be used as reference substance e.g. to validate the linearity of the T-siloxane signals in ^{29}Si NMR.
- **Toluene** (CAS 108-88-3; purity: > 99,8 %; water < 0,01 %)

A.7 Procedure

A.7.1 Sample preparation

a) Standard version: dissolve approx. 2,5 mL sample in approx. 1 mL toluene/C_6D_6 mixture (1:1) with 1 % $Cr(acac)_3$ in a 10 mm NMR tube and homogenize the mixture.

b) Variant: dissolve approx. 150 mg sample in approx. 0,7 mL CD_2Cl_2 with 1 % $Cr(acac)_3$ in a 5 mm NMR tube and homogenize the mixture.

c) Chemical shifts calibration with TMS as internal standard: Add 5 mg to 10 mg of TMS to the samples prepared according to procedures a) or b).

NOTE $Cr(acac)_3$ is the relaxation reagent. Without the addition of toluene, $Cr(acac)_3$ can be precipitated.

A.7.2 Measurement procedure

NMR measurements should be performed according to the user manuals/guidelines provided by manufacturer of the technical equipment.

A.8 Evaluation

A.8.1 Analysis of results

For data processing and analysis (peak positions, integration, etc.) use commercially available software, e.g., provided by the technical manufacturers (Bruker Topspin or similar). For appropriate analysis, the signal to noise ratio shall be (S/N) of 1 000:1.

1) If Tetramethylsilane (TMS) is added as internal standard, reference the respective signal as δ = 0,0 ppm for spectra calibration. If no TMS is added, reference the most intense signal in the M range to +6,750 ppm.
2) Integrate each individual signal within the following shift regions (see Table A.1):
   - M-units ($Me_3SiO_{1/2}$): +12 ppm up to +5 ppm
   - D-units ($Me_2SiO_{2/2}$): −8 ppm up to −24 ppm
   - T-units ($MeSiO_{3/2}$): −40 ppm to −68 ppm

Table A.1 – Shift regions and assignment

Integral	From [ppm]	Up to and including [ppm]	Assignment
A	14,8	14,4	M(OR)
B	8,7	5,5	M
C	0,4	−2,3	SiC_4
D	−8,4	−10,3	D_3
E	−12,0	−13,0	D(OR)
F	−18,6	−20,6	D_4
G	−20,6	−23,9	D
H	−57,4	−57,5	T
I	−58,1	−58,8	T
J	−64,3	−64,9	T
K	−65,2	−68,1	T

NOTE "SiC_4" refers to Si atoms that are surrounded by four C atoms.

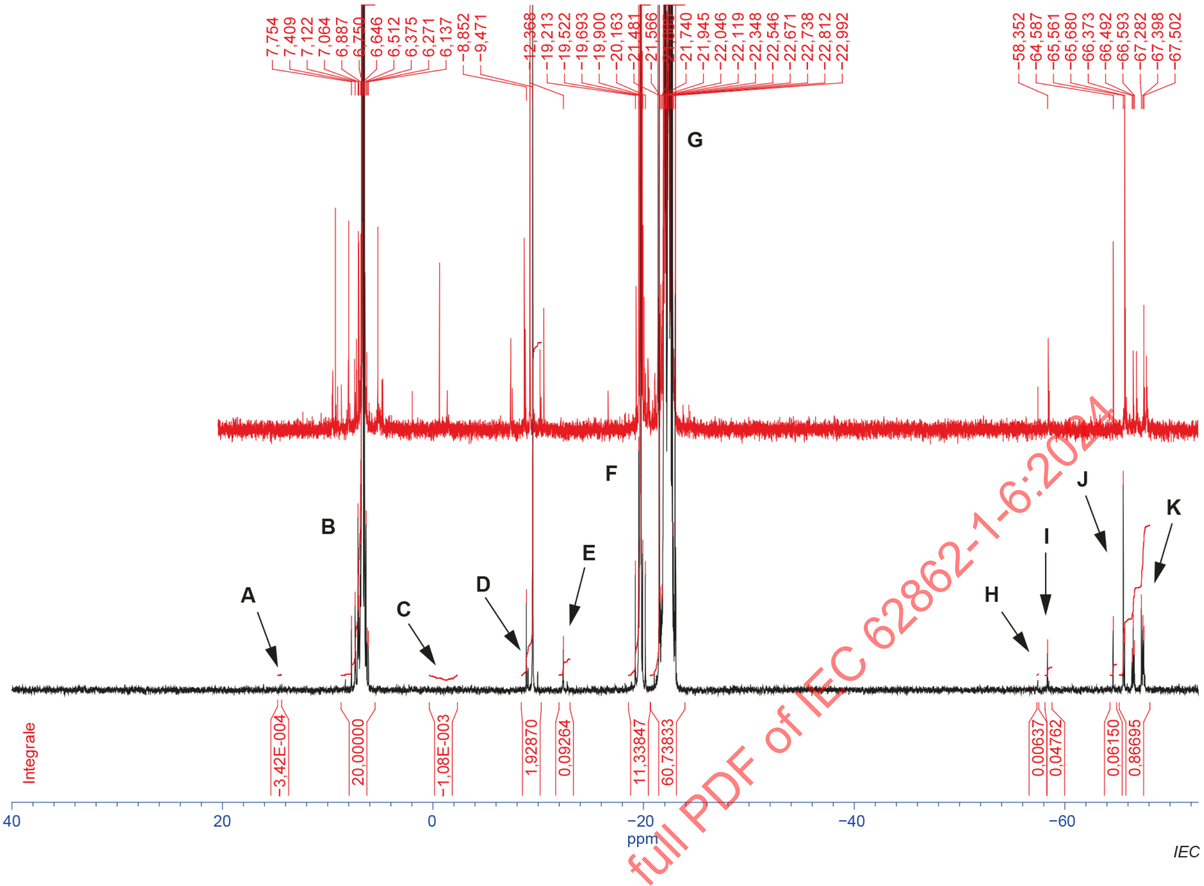

Figure A.5 – Representation of a ^{29}Si NMR spectrum indicating the different shift regions

A.8.2 Calculation of the degree of degradation

As signal intensity is proportional to the amount of ^{29}Si nuclei, the molar ratio of $M{:}D{:}T$ can be determined by comparing the integral sums of each shift region defined in Figure A.6.

1) Sum up all integrals of each shift region as well as the total.

   $\sum I_\mathrm{M}$; $\sum I_\mathrm{D}$; $\sum I_\mathrm{T}$

   $\sum I_\mathrm{all} = \sum I_\mathrm{M} + \sum I_\mathrm{D} + \sum I_\mathrm{T}$

2) Divide each integral sum by the total for scaling

   $\sum I_i \,/\, \sum I_\mathrm{all} \times 100 = i\ \%\ (i = M, D, T)$

3) Set up the scaled $M{:}D{:}T$ ratio for quantifying the degree of degradation.

   The unit of the calculated value is mole percent (mol-%).

4) To calculate the growth rate of a random year, subtract the determined amount of T-groups (mol-%) of the certain year $\sum I_\mathrm{T}\ (i)$ from its previous year $\sum I_\mathrm{T}\ (i{-}1)$.

The maximum amount of T-groups tolerable in the SiHTF and the typical mean annual T-group growth rate at a specific temperature shall be given by the HTF manufacturer or supplier.

A.8.3 Assessment of the result

Determine the amount of T-groups via ^{29}Si NMR spectroscopy before and after thermal exposure. Note that the amount of T-groups after filling the system in a cold state is the initial value. The changes in the T-group amount of the heat transfer fluid shall be taken as a percentage of the M:D:T ratio (mean of at least three samples). The test temperature and test period shall be reported for every T-group amount. The lower the percentage of T-units (the lower the degree of decomposition with the same test temperature and test period), the greater is the thermal stability of a heat transfer fluid.

As small values show a greater deviation than higher amounts of T-group it is necessary to evaluate the aging in the first years of operation over a period of minimum 5 (five) years in a row for a reliable evaluation of the average aging rate.

A.9 Accuracy

A.9.1 General

To validate the quantification of T-groups via ^{29}Si NMR – with respect to ISO 10012 – samples shall be measured at different spectrometers and analysed by different operators. Furthermore, a dilution series with a defined T-group containing standard should be performed to show the accuracy and linearity of this method.

A.9.2 Addition of TM$_3$ as external standard

TM$_3$ is a monodisperse and well-defined siloxane compound consisting of one T-unit and three M-units. ^{29}Si-NMR renders its molecular ratio: 74,75 mol % M, 25,25 mol % T). Hence, this substance can be used as an external standard to verify the measured T-groups.

As an external standard, TM$_3$ should be added to a SiHTF sample in a dilution series between < 0,1 mol % and 1,0 mol % T-units. In both cases the results should demonstrate the accuracy of ^{29}Si NMR by linearity between added TM$_3$ (in mol %) and the measured amount (also in mol %). Furthermore, 0,1 mol % in general can be set as an acceptable detection limit for T-groups when using a representative 500 MHz NMR spectrometer.

A.9.3 Repeatability

To demonstrate the repeatability of ^{29}Si NMR measurements a selected SiHTF sample should be consecutively measured three times at different spectrometers and analyzed with identical integral patterns.

A.9.4 Reproducibility

To evaluate the reproducibility of this method the deviation of different spectrometers as well as different operators should be investigated.

A.10 Example with TM$_3$ as reference substance

TM$_3$ is a monodisperse T-based siloxane with an M:T-ratio of 3:1 (see Figure A.6).

δ (^{29}Si) = 7,5 (3Si, $Me_3SiO_{1/2}$) and −64,3 (1Si, $MeSiO_{3/2}$) ppm.

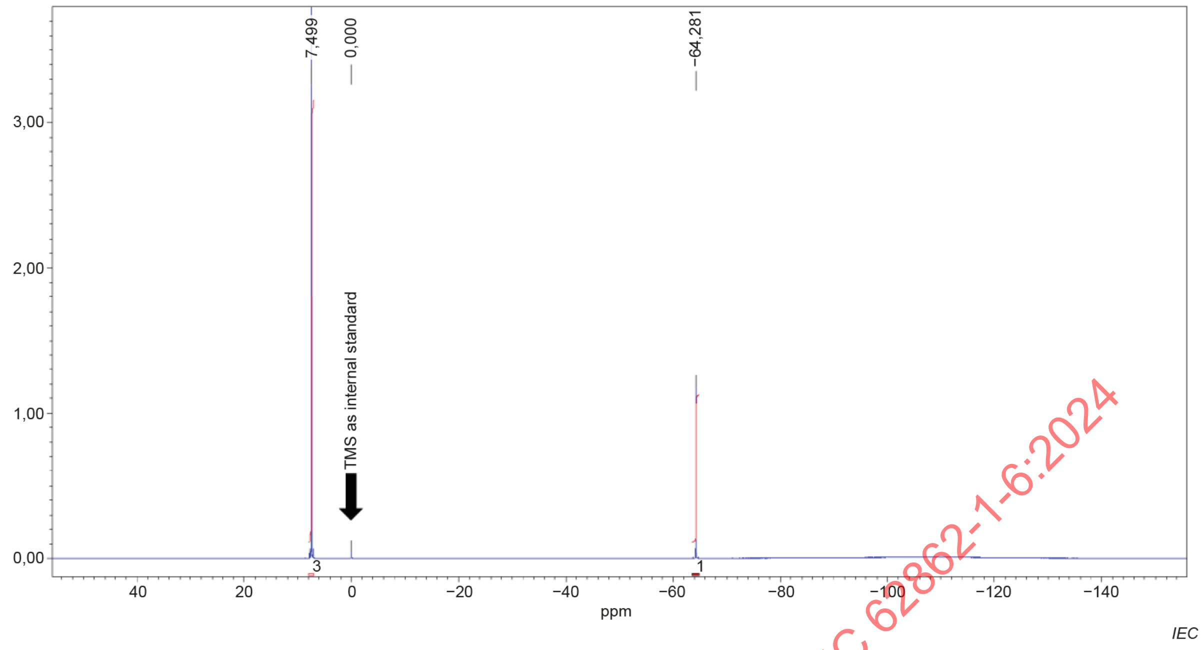

Figure A.6 – ^{29}Si NMR spectrum (99,3 MHz, CD_2Cl_2) of TM_3 with TMS as internal standard

Calculate the M:T ratio as shown in A.8.2:

$\sum I_\mathrm{M}$ = 3,0; $\sum I_\mathrm{T}$ = 1,0; $\sum I_\mathrm{all}$ = 4,0

$\sum I_\mathrm{M} / \sum I_\mathrm{all}$ = 3,0/4,0 × 100 = 75,0 % M; $\sum I_\mathrm{T} / \sum I_\mathrm{all}$ = 1,0/4,0 × 100 = 25,0 % T

M:T = 75,0: 25,0 (all mol-%)