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Water quality — Determination of cyclic volatile methylsiloxanes in water —

Part 1: Method using purge and trap with gas chromatography-mass spectrometry (GC-MS)

Qualité de l'eau — Détermination des méthylsiloxanes cycliques volatiles dans l'eau —

Partie 1: Méthode par dégazage et piégeage avec chromatographie en phase gazeuse-spectrométrie de mass (GC-MS)

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Foreword

ISO (the International Organization for Standardization) is a worldwide federation of national standards bodies (ISO member bodies). The work of preparing International Standards is normally carried out through ISO technical committees. Each member body interested in a subject for which a technical committee has been established has the right to be represented on that committee. International organizations, governmental and non-governmental, in liaison with ISO, also take part in the work. ISO collaborates closely with the International Electrotechnical Commission (IEC) on all matters of electrotechnical standardization.

The procedures used to develop this document and those intended for its further maintenance are described in the ISO/IEC Directives, Part 1. In particular the different approval criteria needed for the different types of ISO documents should be noted. This document was drafted in accordance with the editorial rules of the ISO/IEC Directives, Part 2 (see www.iso.org/directives).

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Any trade name used in this document is information given for the convenience of users and does not constitute an endorsement.

For an explanation on the voluntary nature of standards, the meaning of ISO specific terms and expressions related to conformity assessment, as well as information about ISO's adherence to the World Trade Organization (WTO) principles in the Technical Barriers to Trade (TBT) see the following URL: www.iso.org/iso/foreword.html.

This document was prepared by Technical Committee ISO/TC 147, *Water quality*, Subcommittee SC 2, *Physical, chemical and biochemical methods.*

A list of all parts in the ISO 20596 series can be found on the ISO website.

Water quality — Determination of cyclic volatile methylsiloxanes in water —

Part 1: Method using purge and trap with gas chromatography-mass spectrometry (GC-MS)

WARNING — Persons using this document should be familiar with normal laboratory practice. This document does not purport to address all of the safety problems, if any, associated with its use. It is the responsibility of the user to establish appropriate safety and health practices.

IMPORTANT — It is absolutely essential that tests conducted in accordance with this document be carried out by suitably qualified staff.

1 Scope

This document specifies a method for the quantitative determination of selected cyclic volatile methylsiloxanes (cVMS) in non-filtered water samples by purge and trap extraction with isotope dilution gas chromatography-mass spectrometry (GC-MS).

This method is applicable to the determination of individual cVMS, including:

— octamethylcyclotetrasiloxane (D4);

— decamethylcyclopentasiloxane (D5);

— dodecamethylcyclohexasiloxane (D6);

in surface water, ground water, and wastewater. It can be applied to samples within the concentration range of 0,01 µg/l to 1 µg/l of each of the target compounds. Depending on the matrix, the method may also be applicable to higher concentrations ranging from 1 µg/l to 100 µg/l after suitable dilution of the sample or reduction in sample size.

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.

ISO 3696, *Water for analytical laboratory use — Specification and test methods*

ISO 4793, *Laboratory sintered (fritted) filters — Porosity grading, classification and designation*

ISO 5667-4, *Water quality — Sampling — Part 4: Guidance on sampling from lakes, natural and man-made*

ISO 5667-6, *Water quality — Sampling — Part 6: Guidance on sampling of rivers and streams*

ISO 5667-10, *Water quality — Sampling — Part 10: Guidance on sampling of waste waters*

ISO 5667-11, *Water quality — Sampling — Part 11: Guidance on sampling of groundwaters*

ISO 8466-1, *Water quality — Calibration and evaluation of analytical methods and estimation of performance characteristics — Part 1: Statistical evaluation of the linear calibration function*

3 Terms and definitions

No terms and definitions are listed in this document.

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

— ISO Online browsing platform: available at https://www.iso.org/obp

— IEC Electropedia: available at https://www.electropedia.org/

4 Principle

Extraction of the analytes listed in Table 1 from the water sample by purge and trap extraction, solvent elution and determination by gas chromatography with mass spectrometric detection.

Table 1 — Analytes determinable by this method

Analyte	Formula	Abbreviation	CAS-RN[a]
Octamethylcyclotetrasiloxane	$C_8H_{24}O_4Si_4$	D4	556–67–2
Decamethylcyclopentasiloxane	$C_{10}H_{30}O_5Si_5$	D5	541–02–6
Dodecamethylcyclohexasiloxane	$C_{12}H_{36}O_6Si_6$	D6	540–97–6

[a] CAS-RN: Chemical Abstracts Services Registration Number.

5 Interferences

WARNING — Silicone includes D4, D5 and D6, and is widely used in consumer products such as hair care products, cosmetics, hand lotions, and antiperspirant. As silicone is present in many consumer products, the user should take care not to use hand lotions or other possible sources of contamination before or during the sampling and analysis. Pay special attention to avoid any contamination.

5.1 General

Contamination introduced during the analytical procedure is monitored by the determination of blanks (see 9.3).

5.2 Interferences with sampling and extraction

Sampling containers shall consist of materials that do not change the composition of the sample during sample storage. All types of silicone polymer materials shall be avoided during sampling, sample storage and extraction. Sample containers shall be rinsed thoroughly with acetone (6.2) and *n*-hexane (6.3) prior to use. Sample containers shall be checked for possible background contamination before use when a new type of bottles is prepared.

5.3 Interferences with GC-MS

Silicones are also commonly found in parts and consumables associated with gas chromatography including septa for the vials and inlet. Additionally, GC columns are polydimethysiloxane based and when exposed to moisture and heat also contribute to background cVMS. Autosampler vial septa should be silicone free or thinly coated with PTFE (PTFE = polytetrafluoroethene) on the side exposed to the sample. The inlet septum should be replaced with a Merlin Microseal™[1)] to reduce background contamination from this source. Also any solvents should be dried prior to injection into the GC or care should be taken to use a solvent in which water is only soluble in the ppm levels.

1) Merlin Microseal is the trademark of a product. This information is given for the convenience of users of this document and does not constitute an endorsement by ISO of the product named. Equivalent products may be used if they can be shown to lead to the same results.

6 Reagents

Use reagents with negligible concentrations of the compounds of interest compared with the concentrations to be determined and verify by blank determinations and, if necessary, apply additional cleaning steps.

6.1 Water, grade 1, as specified in ISO 3696.

6.2 2-propanone (acetone), C_3H_6O.

6.3 *n*-hexane, C_6H_{14}.

6.4 Sodium sulfate, anhydrous, Na_2SO_4, powdered.

6.5 Individual internal standard stock solutions.

2,4,6,8-$^{13}C_4$-octamethylcyclotetrasiloxane

2,4,6,8,10-$^{13}C_5$-decamethylcyclopentasiloxane

2,4,6,8,10,12-$^{13}C_6$-dodecamethylcyclohexasiloxane

Weigh 10 mg of each compound into separate 100 ml volumetric flasks and make up to the mark with hexane (6.3), to prepare solutions of mass concentration ρ approximately 100 000 µg/l.

6.6 Multiple internal standard stock solutions.

Dilute the individual internal standard stock solutions (6.5) in a volumetric flask with hexane (6.3) in the ratio of 1:10, to prepare a solution of mass concentration ρ approximately 10 000 µg/l.

6.7 Internal standard working solution.

Dilute the internal standard stock solutions (6.5) in a volumetric flask with acetone (6.2) in the ratio of 1:100, to prepare a solution of mass concentration ρ approximately 1 000 µg/l.

6.8 Individual stock solutions of reference compounds of the analytes listed in Table 1.

Weigh 10 mg of each reference compound into a separate 100 ml volumetric flask and make up to the mark with *n*-hexane (6.3), to prepare solutions of mass concentration ρ approximately 100 000 µg/l.

6.9 Multiple reference compounds stock solution.

Dilute the stock solutions (6.8) in a volumetric flask with *n*-hexane (6.3) in the ratio of 1:10, to prepare a solution of mass concentration ρ approximately 10 000 µg/l.

6.10 Calibration standards.

Prepare at least five calibration solutions by appropriate dilution of the multiple reference compounds stock solution (6.9), using *n*-hexane (6.3). Add to each solution the same amount of the multiple internal standard stock solution (6.6) to give a final concentration of ρ approximately 100 µg/l.

Transfer, for example, 100 µl of the multiple reference compounds stock solution (6.9) and the internal standard stock solution (6.6) into a 10 ml volumetric flask and make up to the mark with *n*-hexane (6.3). A volume of 1 µl of this calibration solution contains 100 pg of the respective individual analytes and internal standards.

When the solutions (6.5 to 6.10) are not being used, store the standards in a freezer (below −18 °C) in sealed ampoules or screw-capped vials with PTFE-lined caps (silicone free). Check the concentrations

regularly so that solvent loss by evaporation can be detected. If solvent loss has occurred, replace the solutions.

6.11 Solid phase extraction material.

A styrene-divinylbenzene polymer sorbent, e.g. commercially available packing material, should be used (see Table A.1).

NOTE Other sorbents can be applicable, provided their suitability has been proven.

6.12 Nitrogen, N_2, purity ≥ 99,996 % volume fraction, for purge and trap extraction, for drying of the sorbent packing after sample extraction and for concentration of extracts by evaporation.

7 Apparatus

Equipment or parts which may come into contact with the water sample or the extract should be free from interfering compounds.

Clean all labware and apparatus for purge and trap extraction assembly by rinsing with acetone (6.2) and *n*-hexane (6.3).

7.1 Narrow-neck flat bottomed glass bottles, conical shoulders, of capacity 500 ml, with glass stoppers or with PTFE-lined or silicone polymer-free screw caps.

The bottle, cap liner or glass stopper should be rinsed with acetone (6.2) and *n*-hexane (6.3) and dried before use in order to minimize contamination.

7.2 Balance, capable of weighing to ±0,01 g.

7.3 Solid phase extraction cartridges, inert non-leaching plastic, e.g. polypropylene.

The cartridges should be packed with a minimum of 100 mg of solid phase extraction material (6.11) as sorbent. In general, 100 mg to 300 mg of sorbent (Table A.1) in a single cartridge is sufficient for collecting analytes from the purge gas.

7.4 Volumetric flasks, with inert stopper.

7.5 Purge and trap assembly.

Examples of two types of purge and trap assemblies that can be used are illustrated in Annex B.

Figure B.1 shows a purge and trap extraction assembly which uses a vacuum pump. It consists of a glass gas wash bottle (7.5.1), gas purifiers (7.5.2), solid phase extraction cartridge (7.3), flow meter (7.5.3), connectors (7.5.4), vacuum pump (7.5.5) and ultrasonic water bath (7.5.6).

Figure B.2 shows a purge and trap extraction assembly which uses a nitrogen stream. It consists of a glass gas wash bottle (7.5.1), solid phase extraction cartridge (7.3), flow meter (7.5.3), connectors (7.5.4), and ultrasonic water bath (7.5.6).

7.5.1 Gas wash bottle, 1 l capacity, screw cap type, with a glass filter pore size ranging 16 µm to 40 µm, P40, as specified in ISO 4793.

NOTE Other glass gas filter can be applicable, but they have not been evaluated for this use.

7.5.2 Gas purifiers, capable of removing target compounds from ambient air, e.g. styrene-divinylbenzene polymer sorbent.

7.5.3 Flow meter, with appropriate measurement range, e.g. approximately 2 l/min.

7.5.4 Connectors, use silicone free material.

7.5.5 Vacuum pump, capable of reaching a flow rate of 1 l/min.

7.5.6 Ultrasonic water bath, equipped with a variable temperature water bath capable of maintaining (50 ± 5) °C.

7.6 Evaporation assembly, using a nitrogen (6.12) stream passing through a stainless-steel needle.

7.7 Vials, brown glass with PTFE-lined or fluorocarbon-based rubber septa, capacity, e.g. 1,5 ml, depending on the auto-sampler. Use silicone free material.

7.8 Gas chromatograph/mass spectrometer.

The gas chromatograph shall be temperature-programmable, with all required accessories including gases, capillary columns (Annex C) and capillary injector.

The mass spectrometer should be capable of operating over the mass range of interest and it should be equipped with a data system capable of quantifying ions using selected *m*/*z* values.

8 Sampling and sample preservation

Take samples in accordance with ISO 5667-4, ISO 5667-6, ISO 5667-10 and ISO 5667-11, in suitable containers, preferably directly into a cleaned glass bottle (7.1). It is advisable to take two samples, one to be retained in the event of a repeat analysis being required.

Fill the bottle (7.1), avoiding turbulence, with the water sample without any headspace. Keep the samples away from light.

The water samples should be stored in a cool box immediately after the sampling and during subsequent transportation.

Store the samples in a refrigerator (4 ± 2) °C and analyse as soon as possible. It is recommended that the sample be analysed preferably on the day of sampling, and not later than 4 d after the sampling.

NOTE Guidance on preservation and handling of water samples can be found in ISO 5667-3.

9 Procedures

9.1 Purge and trap extraction

9.1.1 General

Samples are examined without pre-treatment, i.e. suspended solids are not removed prior to analysis.

9.1.2 Conditioning of the solid phase material

Rinse the cartridge (7.3) with 3 ml elution solvent (9.1.4), and let the cartridge dry using a nitrogen stream. Install the cartridge into the purge and trap assembly immediately after the conditioning.

9.1.3 Sample extraction

Start the extraction immediately after conditioning the cartridge.

Weigh the sample bottle using the balance (7.2).

Gently transfer the whole water sample in the sample bottle (about 600 ml) to the glass gas wash bottle (7.5.1 and Annex B), avoiding release of gas bubbles. Rinse the sample bottle and original cap with about 10 ml of water (6.1), then about 4 ml of acetone (6.2). Add both rinses to the glass gas wash bottle. Add 100 µl of the internal standard working solution (6.7) underneath the water level of the sample and set the gas wash bottle to the purge and trap assembly (7.5) after equilibration (about 10 min). Let this sample purge using vacuum pump or nitrogen stream at a sufficient flow rate and purge time, about 1 l/min and 120 min, respectively. Use ultrasonic assistance, at a water bath temperature of about 50 °C in order to have sufficient extraction efficiency. Check the extraction blank regularly (9.3), so that the target breakthrough on the gas purifier, which is installed in purge and trap assembly by vacuum, can be detected. If the target breakthrough has occurred, replace the gas purifier.

NOTE 1 For rinsing the sample bottle in the above conditions, up to 10 ml of acetone can be used. Maximum volume of rinsing solvent can vary depending on extraction conditions, such as type and/or size of trap sorbent.

NOTE 2 Other purge and trap conditions (flow rate, purge time, and water bath temperature) can be applicable, provided their suitability has been proven.

Prepare suitable dilution of the water sample, if the concentration exceeds the working range established by the calibration function. Gently transfer a suitable volume of the water sample (e.g. 50 ml) to the glass gas wash bottle (7.5.1 and Annex B), after adding water (6.1, e.g. 450 ml), avoiding release of gas bubbles. Add the internal standard working solution (6.7) underneath the water level of the sample, then follow the same extraction procedure as described above.

Care should be taken if subsample is prepared by dilution, resulting in a change in the concentration of suspended particle matter in the sample. Before making dilution of the sample, gently homogenize the sample by rotating the sample bottle.

Remove the residual water in the sorbent packing by passing nitrogen through the cartridge (e.g. 1 l/min for 20 min).

Reweigh the empty sample bottle with its original cap or stopper and calculate the net weight of sample by difference to the nearest g. For an assumed density of 1 g/ml, this net weight (in grams) is equivalent to the volume (in millilitres) of water extracted.

9.1.4 Elution

Add sufficient volume *n*-hexane (6.3), e.g. 1,5 ml to the completely dried cartridge, and elute through the cartridge.

Gently concentrate the eluate to 1 ml using the evaporation assembly (7.6).

To remove water from the eluate, add 0,5 g of sodium sulfate (6.4), if necessary.

Transfer the eluate to the suitable vial (7.7).

Instead of *n*-hexane, other organic solvents, e.g. dichloromethane (CH_2Cl_2), may be used if the instrumental blank can be comparable or lower than those of *n*-hexane. If an alternative solvent is used, then it shall be matched when preparing the calibration standard solutions.

9.2 GC-MS operating conditions

Optimize the operating conditions of the GC-MS system in electron ionization mode in accordance to the manufacturers' instructions. Determine the appropriate GC oven temperature programme experimentally during implementation and in-house validation. To ensure optimum sensitivity, selected ions (Table 2) are monitored. An example of operating conditions is given in Annex D.

In order to clean the inlet system free from cVMS, inject *n*-hexane (6.3) at least three times from GC-vials (7.7) before measuring the sample extracts or calibration standard solutions.

In order to reduce GC-MS system blank levels, set the GC inlet temperature in a range between 150 °C and 200 °C.

9.3 Blank determination

Treat the blank in exactly the same manner as the sample, except that the sample replaced by the appropriate amount of water (6.1). Determine the blank level in accordance with Formula (3). At least one blank determination shall be performed prior to analysing real samples, in order to determine the performance of the entire procedure with respect to contamination. The blank level should not exceed one-third of the lowest calibration standard solution or of the lowest level of interest [see Formula (3)]. The maximum allowed blank level for each cVMS is lower than one-third of the lowest level of interest.

Subtract the concentration of the blank from the concentration of the water samples, if it is detectable in GC-MS.

Check the ongoing condition of instruments and reagents by blank determination at regular interval.

If significant amount of the blank is determined or when a new inlet septa on GC is installed, bake the GC inlet at high temperature (e.g. 280 °C) for several hours before use, but do not exceed the maximum temperature limit of GC column.

9.4 Identification

Identify target compounds in the sample by matching both retention times and relative intensities of the diagnostic ions (Table 2) of sample and calibration standard (6.10). It is necessary to use specific pairs of ions (target M_1 and qualifier M_2 in Table 2) for the quantification of each resolved peak.

The target compound is identified as being present in the sample if:

— the relative or the absolute sample component retention time measured in the selected ion current chromatogram matches the relative or absolute retention time of the authentic compound within ±0,2 % (or a maximum of ±6 s) in the chromatogram of corresponding internal standard or those of the latest reference compounds, measured under identical conditions;

— the selected diagnostic ions (see Table 2) are present at the substance specific retention time;

— the relative intensities of all selected diagnostic ions observed for samples shall match the abundance observed for reference compounds to within 25 %. It is important that both of the above criteria be satisfied in order to confirm the presence of a target compound.

Table 2 — Selected diagnostic ions for identification and quantification

No	Analyte	Abbreviation	Selected diagnostic ions	
			Target M_1[a]	Qualifier M_2[b]
1	Octamethylcyclotetrasiloxane	D4	281	265
2	Decamethylcyclopentasiloxane	D5	355	267
3	Dodecamethylcyclohexasiloxane	D6	429	341
4	2,4,6,8-$^{13}C_4$-octamethylcyclotetrasiloxane[c]	$^{13}C_4$-D4	285	268
5	2,4,6,8,10-$^{13}C_5$-decamethylcyclopentasiloxane[c]	$^{13}C_5$-D5	360	270
6	2,4,6,8,10,12-$^{13}C_6$-dodecamethylcyclohexasiloxane[c]	$^{13}C_6$-D6	435	345
[a] M_1 is used for quantification.				
[b] M_2 may be used for identification.				
[c] Internal standard.				