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Water quality — Determination of cyclic volatile methylsiloxanes in water —

Part 2: Method using liquid-liquid extraction with gas chromatography-mass spectrometry (GC-MS)

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

Partie 2: Méthode par extraction liquide-liquide avec chromatographie en phase gazeuse-spectrométrie de masse (CG-SM)

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ISO copyright office
CP 401 • Ch. de Blandonnet 8
CH-1214 Vernier, Geneva
Phone: +41 22 749 01 11
Email: copyright@iso.org
Website: www.iso.org

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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).

Attention is drawn to the possibility that some of the elements of this document may be the subject of patent rights. ISO shall not be held responsible for identifying any or all such patent rights. Details of any patent rights identified during the development of the document will be in the Introduction and/or on the ISO list of patent declarations received (see www.iso.org/patents).

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

For an explanation of 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 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.

Any feedback or questions on this document should be directed to the user's national standards body. A complete listing of these bodies can be found at www.iso.org/members.html.

Introduction

The method described in this document uses low density polyethylene to prevent volatilization of samples during transit and storage. The samples are processed using a liquid-liquid extraction into a non-polar solvent with subsequent injection onto a gas chromatograph-mass spectrometer for separation and quantitation.

Water quality — Determination of cyclic volatile methylsiloxanes in water —

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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 and to ensure neutralization and proper disposal of waste solutions.

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 determination of certain cyclic volatile methylsiloxanes (cVMS) in environmental water samples with low density polyethylene (LDPE) as a preservative and subsequent liquid-liquid extraction with hexane containing ^{13}C-labeled cVMS as internal standards. The extract is then analysed by gas chromatography-mass spectrometry (GC-MS).

NOTE Using the ^{13}C-labeled, chemically identical substances as internal standards with the same properties as the corresponding analytes, minimizes possible substance-specific discrimination in calibrations. Since these substances are least soluble in water, they are introduced via the extraction solvent hexane into the system.

This document is applicable to the measurement of the following cVMS in rivers, streams, and waste water (influent and effluent):

Table 1 — Analytes determined by this method

Analyte	Formula	Abbreviation	CAS[a] -RN
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			

This method can be used to determine cVMS from 0,1 µg/l to 250 µg/l. In well controlled laboratory environments, where contamination is minimized, the lower end of the application range can be diminished by a factor of up to 10.

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 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 5667-14, *Water quality — Sampling — Part 14: Guidance on quality assurance and quality control of environmental water sampling and handling*

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*

ISO/TS 13530, *Water quality — Guidance on analytical quality control for chemical and physicochemical water analysis*

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 http://www.iso.org./obp

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

4 Principle

4.1 Principle of preservation and extraction

The siloxane compounds (D4), (D5), and (D6) are relatively volatile and have low solubility in water thus making accurate quantification in aqueous matrices challenging. Low density polyethylene (LDPE) is added to samples to prevent volatilization of the cVMS through a partial physical barrier between the water and headspace and a matrix to which the cVMS may adsorb. Hexane is then used to extract the dissolved and sorbed fractions of cVMS. The hexane extracts are then analysed by GC-MS (Annex A).

5 Interferences

5.1 Interferences with sampling and processing

Silicones, including D4, D5, and D6 are widely used in industrial applications as well as personal care products such as conditioner, hand lotion, sunscreens, and cosmetics (not all inclusive). Persons involved with the collection and analysis of samples should refrain from using siloxane containing products to limit potential contamination of the sample.

Additionally, the users should refrain from using collection devices, sampling containers, laboratory equipment or consumables which may contain silicones/siloxanes. Sample contact surfaces should be suitably rinsed with acetone or hexane and subsequently dried in a clean area of the laboratory to remove any contamination.

5.2 Interferences with GC-MS

Silicones are also commonly found in parts and consumables associated with gas chromatography including septa for the vials and inlet. Commonly used types of GC columns are polydimethylsiloxane based which when exposed to moisture or when heated may generate cVMS and in such a way can contribute to background. Thus, the use of non-polydimethylsiloxane-based GC columns is highly recommended, in particular when analysing sub-ppb concentrations. Autosampler vial septa should be silicone free or at a minimum coated with polytetrafluoroethylene 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. In addition, 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 mg/l levels.

5.3 Interferences determination

In order to determine the integrity of the sampling, preparation and instrumental analysis of the samples, it is recommended to prepare quality control (QC) samples. An example of QC samples consists of a series of blanks and spikes to identify potential sources of contamination or loss during the life cycle of the samples.

6 Reagents

It is recommended to verify the absence (or presence of only negligible amounts) or absence of cVMS from solvents being utilized.

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

6.2 Hexane, C_6H_{14} *n*-hexane or mixture of isomers, determined to be suitably free of cVMS.

6.3 Tetrahydrofuran, C_4H_8O.

6.4 Calibration stock solutions.

6.4.1 Reference substances

See Table 1.

— Octamethylcyclotetrasiloxane;

— Decamethylcyclopentasiloxane;

— Dodecamethylcyclohexasiloxane.

6.4.2 Calibration stock solution 1

Weigh 30 mg of each of the listed standards into a 25 ml volumetric flask and fill to volume with hexane (6.2). The concentration of this solution is approximately 1 200 µg/ml.

6.4.3 Calibration stock solution 2

Dilute calibration stock solution 1 (6.4.2) with hexane (6.2) in a ratio of 1:250. The concentration of this solution is approximately 4 800 ng/ml.

6.4.4 Calibration stock solution 3

Dilute calibration stock solution 2 (6.4.3) with hexane (6.2) in a ratio of 1:100. The concentration of this solution is approximately 48 ng/ml.

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

6.5 Spiking stock solutions

6.5.1 Spiking stock solution 1

Dilute calibration stock solution 1 (6.4.2) with tetrahydrofuran (6.3) in a ratio of 1:100. The concentration of this solution is approximately 12 µg/ml.

6.5.2 Spiking stock solution 2

Dilute spiking stock solution 1 (6.5.1) with tetrahydrofuran (6.3) in a ratio of 1:50. The concentration of this solution is approximately 240 ng/ml.

6.6 Internal standard working solution

6.6.1 Individual internal standards

^{13}C-labelled cVMS. Typical products available from suppliers are:

— ^{13}C-D4, such as 2,4,6,8-$^{13}C_4$-octamethylcyclotetrasiloxane; or

— 2,2,4,4,6,6,8,8-$^{13}C_8$-octamethylcyclotetrasiloxane;

— ^{13}C-D5, such as 2,4,6,8,10-$^{13}C_5$-decamethylcyclopentasiloxane; or

— or 2,2,4,4,6,6,8,8,10,10-$^{13}C_{10}$-decamethylcyclopentasiloxane;

— ^{13}C-D6, such as 2,4,6,8,10,12-$^{13}C_6$-dodecamethylcyclohexasiloxane.

6.6.2 Internal standard stock solution 1

Weigh 10 mg of the appropriate internal standard (6.6.1) into a 100 ml volumetric flask and fill to volume with hexane (6.2). The concentration of this solution is approximately 100 µg/ml.

6.6.3 Internal standard stock solution 2

Dilute internal standard stock solution 1 (6.6.2) with hexane (6.2) in a ratio of 1:100. The concentration of this solution is approximately 1 000 ng/ml.

6.6.4 Internal standard working solution

Dilute internal standard stock solution 2 (6.6.3) with hexane (6.2) in a ratio of 1:250. The concentration of this solution is approximately 4 ng/ml.

6.7 Calibration standards

Using Table 2 weigh the appropriate amount of calibration stock 2 (6.4.3) or calibration stock 3 (6.4.4) into a 5 ml volumetric flask and dilute to volume with internal standard working solution (6.6.4). Weigh the amount of internal standard working solution added and convert to volume using the density of the solvent used. Table 2 is given as an example, the calibration range can be modified to meet the needs of the samples. It is recommended that at least five calibration standards be used for a calibration curve.

Table 2 — Calibration standards

	Calibration stock	Volume	Target concentration	Target concentration (relative to 50 ml sample)
		µl	ng/ml	µg/l
STD A	3	20	0,19	0,038