INTERNATIONAL STANDARD

ISO 20596-2

First edition
2021-01

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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Foreword

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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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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 —

Part 2:
Method using liquid-liquid extraction 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 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.

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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

Table 2 *(continued)*

	Calibration stock	Volume	Target concentration	Target concentration (relative to 50 ml sample)
		µl	ng/ml	µg/l
STD B	3	50	0,48	0,096
STD C	3	125	1,2	0,24
STD D	3	275	2,6	0,53
STD E	3	550	5,3	1,1
STD F	2	15	14	2,9
STD G	2	25	24	4,8
STD H	2	50	48	9,6
STD I	2	100	96	19,2
STD J	2	300	288	57,6
STD K	2	750	720	144
STD L	2	1 500	1 440	288

7   Apparatus

WARNING — Any surfaces that come into contact with a solution to be analysed should be suitably rinsed with acetone or hexane and allowed to dry in a clean area of the laboratory to remove any contamination.

7.1   Gas chromatograph/mass spectrometer

The gas chromatograph shall be temperature-programmable, with all required accessories including gasses, capillary columns, autosampler, and mass spectrometric detector. The inlet should be equipped with a Merlin MicroSeal™[2] to minimize contamination (5.2).

The mass spectrometer should be capable of operating over the mass range of interest (200 m/z to 500 m/z) and it should be equipped with a data system capable of quantifying ions using selected m/z values.

7.2   GC columns

Recommended column is DB-WAXetr[3] (30 m × 0,25 mm i.d., 0,25 µm film thickness). If blank levels are proved to be sufficiently low, other columns may be used such as DB-5ms[4], if appropriately tested prior to sample processing.

7.3   **Volumetric flasks**, with inert/silicone free stopper.

7.4   **Vials**, glass autosampler vials with a fluorocarbon lined, non-silicone septa.

7.5   **Multi-Tube Vortexer**[4], capable of handling multiple 125 ml jars.

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2)   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.

3)   DB-WAXetr and DB-5ms are the tradenames of products supplied by Agilent Technologies. 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.

4)   Multi-Tube Vortexer is the tradename of a product available commercially. This information is given for the convenience of users of this document and does not constitute and endorsement by ISO of this product.

7.6   Jars, 125 ml wide mouth glass jars with a PTFE lined lid.

7.7   Centrifuge, Alternative phase separation can be obtained by centrifuging the samples for 5 min at 2 500 rpm.

7.8   Low density polyethylene (LDPE), 51 μm to 63 μm thick clear base film. Film is cut into 2,5 cm × 2,5 cm squares and subsequently washed twice with hexane (6.2) and allowed to dry.

8   Method detection limits

Any laboratory performing this test will determine the limit of detection and the limit of quantification as defined in ISO/TS 13530. The method detection limit and limit of quantification should be assessed as defined in Annex B.

9   Quality control

Quality control samples shall be used to verify the integrity of the samples during sampling, processing and analysing by indicating any potential contamination or loss of analyte (ISO 5667-14). This is most important when analysing concentrations in the sub-μg/l range, where relevant contamination with cVMS is more likely. Typically, a series of blanks and spiked samples are used for quality control. Reference examples of these quality control samples, and their use are described in Annex C.

NOTE   The initial interlaboratory trial conducted when developing this document, for sub-ppb concentrations did not meet the ISO performance criteria, mainly because of an un-discovered contamination issue.

Blank levels and sample concentrations shall differ sufficiently to qualify sample concentrations as relevant. Where concentrations reported are close to the detection limits, replicates of blank samples and of actual samples may be measured and 2-sample t-test can be used to check for a statistically significant difference.

10 Sampling and storage

10.1 Sampling preparation

Ensure that all sample contact surfaces have been washed with acetone or hexane and allowed to dry. And ensure that all LDPE squares have been solvent washed with hexane in duplicate and allowed to dry.

Add 8 LDPE squares to each 125 ml uniquely labelled sample jar with lid. Take a weight of the sample jar. This weight will be used to later determine the weight and volume of the sample.

10.2 Sample collection

Take samples in accordance with ISO 5667-4, ISO 5667-6, ISO 5667-10, ensure sampling collection devices are clean and free of siloxanes. In order to collect a homogenous sample, the sample collection device should be sufficient to contain a bulk sample so that sufficient replicate samples can be poured or drawn from the same source. It is advisable to take two samples, one to be retained in the event of a repeat analysis is required.

If field blanks are utilized, it is appropriate to open the field blanks as described in Annex C.

Rinse the sampling device three times with the intended sample and collect the bulk sample. Then aliquot the bulk sample into the 125 ml sample jars so that each jar is approximately ½ full. This allows for the solvent extraction step to be performed in the jar. The LDPE helps prevent volatilization of cVMS into the headspace.

Close the samples and place them in a storage/shipping container to be maintained at a temperature (5 ± 3) °C. These samples should be extracted within 14 d of collection.

11 Extraction and analysis

11.1 Extraction

Weigh the sample jar to determine the amount of sample collected. Add 10 ml of internal standard working solution (6.6.4) to the samples. The samples are placed on the Multi-Tube Vortexer (7.5) and vortexed at maximum speed for 30 min. The extracted sample in the jar is allowed to settle to separate the organic phase, showing clear phase separation, or alternatively phase separation can be obtained by centrifuging (7.7) the samples. The organic phase is removed and placed in a previously cleaned storage vial. An aliquot is removed from the storage vial and placed into an autosampler vial for analysis by GC-MS.

NOTE   To reduce negative effects caused by water traces being present in the organic phase, it can be advantageous to add approximately 1 g of dry $MgSO_4$ into the vial.

11.2 GC conditions and operation

Example operating conditions can be found in Annex A.

If multiple injections of a sample, blank, or calibration solution are to be made, it is recommended to prepare an autosampler vial for each injection to reduce spurious contamination. It is also recommended to utilize the autosamplers needle wash function prior to and after each sample injection with a wash of hexane.

Solvent blanks and a calibration solution should be run at intervals not to exceed more than ten sample injections to verify the validity of the calibration curve as well as to ensure the background of the instrument is low.

12 Calibration

Example operating conditions can be found in Annex A.

12.1 General requirements

For practical reasons, the calibration uses at least five solutions containing the analytes of interest and internal standards (Annex A and Table 2).

Ensure there is a linear dependence between signal and concentration.

Determine the linear working range using at least five measurements at different concentrations, as specified in ISO 8466-1.

The calibration function for a substance is valid only for the measured concentration range. Additionally, the calibration function depends on the condition of the instrument and shall be checked regularly.

Table 3 — Explanation of subscripts

Subscript	Meaning
a	Target compound
e	Calibration step
I	Internal standard
c	Calibration standard
t	Sample
n	Procedure blank

12.2 Calibration calculations

The purpose of using the internal standard is to account for any errors that can occur during the injection of the sample into the GC. An internal standard can also account for any volatilization occurring during and after the extraction, matrix effects. The internal standard normalizes the results for any of these areas.

The amount in mass of both the internal standard and target compound shall be calculated for each calibration standard.

Plot the values of the ratio y_a/y_I (peak areas, peak heights or integration units) for each substance a on the ordinate and the associated ratio of the added mass m_a/m_I on the abscissa.

Determine the linear regression function using the corresponding pairs of values y_a/y_I and m_a/m_I of the measured series in accordance with Formula (1) or Formula (2):

$$\frac{y_{ac}}{y_{ilc}} = s_{al} \frac{m_{ac}}{m_{ic}} + b_{al} \tag{1}$$

$$\frac{y_{ac}}{y_{ilc}} = s_{al} \frac{m_{ac}}{m_{ic}} \tag{2}$$

where

y_a is the dependent variable corresponding to the measured response, expressed in units which will depend on the method, for example area value, for a given ρ_a of target compound a in the calibration;

y_I is the dependent variable corresponding to the measured response, expressed in units which will depend on the method, for example area value, for a given ρ_I of internal standard I in the calibration;

m_a is the independent variable corresponding to the added mass, expressed in micrograms, of the substance a in the calibration solution;

m_I is the independent variable corresponding to the added mass, expressed in micrograms, of the internal standard I in the calibration solution;

s_a is the slope of the calibration curve from y_a/y_I as a function of the mass ratio m_a/m_I, often called the response factor;

b_{aI} is the ordinate intercept of the calibration.

The decision on the use of the calibration function with Formula (1) or without intercept [Formula (2)] depends on the actual situation. The decision should be taken by the analyst, considering the calibration range, its response to the concentration, and the variance of the data registered, all influenced by the equipment used and instrument set-up.

The analyst should carefully decide whether to use weighting factors proportional to the inverse of the signal intensity (here peak area ratio y_{ac}/y_{ilc}) or to the inverse of sample concentration (in many chromatographic data systems indicated as $\sim 1/y$ or $\sim 1/x$). By doing so, the regression procedure is more focused on low concentrations and less dominated by the higher concentrations and thus compensates the heteroscedastic nature of the data scatter around the regression line in chromatographic methods.

12.3 Concentration calculations

Determine the result of each sample using the prepared calibration curve (11.2). The same procedure should always be used for calibration, but the concentration of the calibration solutions will depend on the sample set being analysed as the samples should fall within the calibration curve. The suitability of the calibration curve should be checked regularly during a run to verify suitability. This may be

accomplished by analysing a calibration solution after every ten sample injections. If the calibration check differs by more than 20 % of the expected value, the data should be reviewed for background contamination, carryover, or instrumental changes. A recalibration of the instrument may be considered.

12.4 Calculation of results

Calculate the mass concentration ρ_a of target compound a in accordance with Formula (3) after solving Formulae (1) or (2). If using Formula (2) then b_{aI} = zero is used. In a stable laboratory environment, the contribution m_n in the denominator of Formula (3), representing the procedure blank n, should be subtracted.

$$\rho_a = \frac{\left\{\frac{\left[\frac{y_{at}}{y_{It}} - b_{aI}\right]}{s_{aI}} \times m_{It}\right\} - m_n}{v_t} \quad \text{with } m_n = \left\{\frac{\left[\frac{y_{an}}{y_{In}} - b_{aI}\right]}{s_{aI}} \times m_{In}\right\} \text{ or } m_n = 0 \tag{3}$$

where

ρ_a　is the mass concentration of the sample expressed in micrograms per litre, μg/l;

y_{at}　is the dependent variable corresponding to the measured response, expressed in units which will depend on the method, for example area value, for a given ρ_a of target compound a in the sample;

y_{It}　is the dependent variable corresponding to the measured response, expressed in units which will depend on the method, for example area value, for a given ρ_i of internal standard I in the sample;

b_{aI}　is the ordinate intercept of the calibration;

s_a　is the slope of the calibration curve from y_{ac}/y_{Ic} as a function of the mass ratio m_{ac}/m_{Ic}, often called the response factor;

m_{It}　is the added mass, expressed in micrograms, of the internal standard I in the sample solution;

m_n　is the mass, expressed in micrograms, of the substance a in the blank solution;

v_t　is the volume of the sample, expressed in L, either determined by direct measurement of the sample or calculated as a function of the sample weight and its density;

y_{an}　is the measured response, expressed in units which will depend on the method, for example area value, for a given ρ_a of target compound a in the procedural blank;

y_{In}　is the measured response, expressed in units which will depend on the method, for example area value, for a given ρ_I of internal standard I in the procedure blank;

m_{In}　is the added mass, expressed in micrograms, of the internal standard I in the procedure blank.

12.5 Treatment of results lying outside the calibration range

If the concentrations of the target compound in the sample lie outside of the range of the calibration curve, either demonstrate a larger linear calibration range or dilute the sample with additional internal standard working solution (6.6.4) by a suitable factor to bring the results within the curve. Calculate the mass concentration ρ_a of target compound a in accordance with Formula (3) after solving Formula (1) or Formula (2). This calculation subtracts the contribution of the procedure blank n from the results.

13 Expression of results

Report the results of compounds listed in Table 1 in micrograms per litre, µg/l, to two significant figures as x,x µg/l.

14 Test report

The test report shall contain at least the following information:

a)   the test method used, together with a reference to this document, i.e. ISO 20596-2:2021;

b)   identification of the sample;

c)   the sample storage and pre-treatment protocol;

e)   details of any deviation from the procedure specified and of all circumstances that may have influenced the results;

f)   the date of the analysis.

The method performance of this document is presented in Annex D.

Annex A
(informative)

GC-MS conditions

Column	DB-WAXetr[a] (30 m × 0,25mm, 0,25 μ film)
Injection size	4 μl
Inlet septum	Merlin MicroSeal™[b]
Inlet temperature	150 °C
Inlet pressure (constant)	124 kPa (18 psi)
Inlet mode	Splitless (5 ml/min at 0,1 min)
Oven temperature	40 °C for 3 min, 40 °C/min to 150 °C, no hold, 60 °C/min to 240, no hold
Transfer line temperature	260 °C
MS source temperature	230 °C
MS quad	150 °C

Selected ions in electron ionization mode Table A.1
(dwell time 20 ms)

[a] DB-WAXetr is the tradename of products supplied by Agilent Technologies. 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.

[b] 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.

Table A.1 — Analytes and selected ions

Analyte	Abbreviation	Selected diagnostic ions	
		Target M$_1$[a]	Qualifier M$_2$[b]
Octamethylcyclotetrasiloxane	D4	281	265
Decamethylcyclopentasiloxane	D5	355	267
Dodecamethylcyclohexasiloxane	D6	429	341
For the ^{13}C-labelled internal standard materials, the ions to be selected depend on the degree of ^{13}C labelling available from the supplier. Typical ions are:			
2,4,6,8-^{13}C$_4$-octamethylcyclotetrasiloxane[c]	^{13}C$_4$-D4	285	268
2,2,4,4,6,6,8,8-^{13}C$_8$-octamethylcyclotetrasiloxane[c]	^{13}C$_8$-D4	289	288 or 271
2,4,6,8,10-^{13}C$_5$-decamethylcyclopentasiloxane[c]	^{13}C$_5$-D5	360	270
[a] M1 is used for quantification			
[b] M2 may be used for identification			
[c] Internal standard			

Table A.1 *(continued)*

Analyte	Abbreviation	Selected diagnostic ions	
		Target M_1[a]	Qualifier M_2[b]
2,2,4,4,6,6,8,8,10,10-$^{13}C_{10}$-decamethylcyclopentasiloxane[c]	$^{13}C_{10}$-D5	365	272
2,4,6,8,10,12-$^{13}C_6$-dodecamethylcyclohexasiloxane[c]	$^{13}C_6$-D6	435	345
[a] M1 is used for quantification			
[b] M2 may be used for identification			
[c] Internal standard			

Annex B
(informative)

Method detection limit and limit of quantification

The method detection limit (MDL) is defined as the minimum level of analyte in a sample matrix, that when processed through the complete analytical method, can be measured and reported with 99 % probability that it is greater than zero and is calculated as $t_{n-1(\alpha 1\ =\ 0,01)} \times s$ where s is the standard deviation of seven replicate preparations and analysis of effluent.

The limit of quantification of a method is defined as the minimum level of analyte in a sample matrix that can be measured and accurately quantified with an uncertainty no greater than 30 % with 99 % probability which was calculated as 2,5 times the MDL.