INTERNATIONAL STANDARD

ISO 18073

First edition
2004-04-15

Water quality — Determination of tetra- to octa-chlorinated dioxins and furans — Method using isotope dilution HRGC/HRMS

Qualité de l'eau — Dosage des dioxines et furanes tétra- à octachlorés — Méthode par dilution d'isotopes HRGC/SMHR

Reference number
ISO 18073:2004(E)

ISO copyright office
Case postale 56 • CH-1211 Geneva 20
Tel. + 41 22 749 01 11
Fax + 41 22 749 09 47
E-mail copyright@iso.org
Web www.iso.org

Published in Switzerland

Contents

Page

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.

International Standards are drafted in accordance with the rules given in the ISO/IEC Directives, Part 2.

The main task of technical committees is to prepare International Standards. Draft International Standards adopted by the technical committees are circulated to the member bodies for voting. Publication as an International Standard requires approval by at least 75 % of the member bodies casting a vote.

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.

ISO 18073 was prepared by Technical Committee ISO/TC 147, *Water quality*, Subcommittee SC 2, *Physical, chemical and biochemical methods*.

Water quality — Determination of tetra- to octa-chlorinated dioxins and furans — Method using isotope dilution HRGC/HRMS

WARNING — Persons using this International Standard should be familiar with normal laboratory practice. This standard 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 compliance with any national regulatory conditions.

Attention is drawn to any relevant national safety regulations. The 2,3,7,8-chloro-substituted PCDDs/PCDFs are among the most toxic of chemicals. All work with PCDDs/PCDFs requires, therefore, the utmost care; the national safety measures which correspond to those for toxic substances shall be strictly adhered to.

1 Scope

This International Standard specifies a method for the determination of tetra- to octa-chlorinated dibenzo-*p*-dioxins (PCDDs) and dibenzofurans (PCDFs) in waters and waste waters (containing less than 1 % by mass solids) using high-resolution gas chromatography/high-resolution mass spectrometry (HRGC/HRMS).

This International Standard is applicable to the seventeen 2,3,7,8-substituted PCDDs/PCDFs specified in Table 1.

The detection limits and quantitation levels in this method are usually dependent on the level of interferences rather than instrumental limitations. The minimum levels (MLs) specified in Table 2 are the levels at which the PCDDs/PCDFs can be determined with no interferences present. The method detection limit (MDL) for 2,3,7,8-TCDD has been determined as 4,4 pg/l based on this method using a sample volume of 1 l. Lower detection limits may be achieved by using a larger sample volume.

This method is “performance based”. The analyst is permitted to modify the method to overcome interferences or lower the cost of measurements, provided that all performance criteria in this International Standard are met. The requirements for establishing method equivalency are given in 9.1.2.

2 Normative references

The following referenced documents are indispensable for the application 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 3696:1987, *Water for analytical laboratory use — Specification and test methods*

ISO 5667-1, *Water quality — Sampling — Part 1: Guidance on the design of sampling programmes*

ISO 5667-2, *Water quality — Sampling — Part 2: Guidance on sampling techniques*

ISO 6879:1995, *Air Quality — Performance characteristics and related concepts for air quality measuring methods.*

3 Terms, definitions and abbreviated terms

3.1 Terms and definitions

For the purposes of this document, the terms and definitions given in ISO 6879:1995 and the following apply.

3.1.1
analyte
PCDD or PCDF tested for by this method

Note See Table 1 for a list of compounds.

3.1.2
calibration standard
solution prepared from a secondary standard and/or stock solutions and used to calibrate the response of the instrument with respect to analyte concentration

3.1.3
calibration verification standard
midpoint calibration standard that is used to verify calibration

3.1.4
congener
any one of the 210 individual PCDDs/ PCDFs

3.1.5
internal standard
$^{13}C_{12}$-labelled 2,3,7,8-PCDD/PCDF analogue added to samples prior to extraction against which the concentrations of native PCDDs and PCDFs are calculated

3.1.6
keeper
high boiling-point solvent added to the sampling standard solution

3.1.7
method blank
aliquot of reagent water that is treated exactly as a sample through the complete analytical procedure including extraction, clean-up, identification and quantification including all the relevant reagents and materials

3.1.8
operational performance characteristics
influence of the physical and chemical environment and maintenance problems, for example; mains voltage, temperature, supply of certain substances, set-up time, period of unattended operation

[See ISO 6879:1995]

3.1.9
pattern
chromatographic print of any series of PCDD/PCDF isomers

3.1.10
PCDD/PCDF isomers
PCDDs or PCDFs with identical chemical compositions but different structures

3.1.11
profile
graphic representation of the sums of the isomer concentrations of the PCDDs and the PCDFs

3.1.12
recovery standard
$^{13}C_{12}$-labelled 2,3,7,8-chloro-substituted PCDD/PCDF, added before injection into the GC

3.1.13
spiking
addition of $^{13}C_{12}$-labelled PCDD/PCDF standards

3.1.14
statistical performance characteristics
quantification, for measured values, of the possible deviations resulting from the random part of the measuring process, e.g. repeatability or instability

[See ISO 6879:1995]

3.2 Abbreviated terms

DCDPE	decachlorodiphenyl ether
GC/MS	gas chromatography/mass spectrometry
GPC	gel-permeation chromatography
HpCDD	heptachlorodibenzo-*p*-dioxin
HpCDF	heptachlorodibenzofuran
HpCDPE	heptachlorodiphenyl ether
HPLC	high-performance liquid chromatography
HRGC	high-resolution gas chromatography
HRMS	high-resolution mass spectrometry
HxCDD	hexachlorodibenzo-*p*-dioxin
HxCDF	hexachlorodibenzofuran
HxCDPE	hexachlorodiphenyl ether
MDL	method detection limit
ML	minimum level (see Table 2)
NCDPE	nonachlorodiphenyl ether
OCDD	octachlorodibenzo-*p*-dioxin
OCDF	octachlorodibenzofuran
OCDPE	octachlorodiphenyl ether
PCDD/PCDF	polychlorinated dibenzo-*p*-dioxin/dibenzofuran
PeCDD	pentachlorodibenzo-*p*-dioxin
PeCDF	pentachlorodibenzofuran

PTFE polytetrafluoroethylene

SIM selected ion monitoring

TCDD tetrachlorodibenzo-*p*-dioxin

T**C**DF tetrachlorodibenzofuran

TEF toxic equivalent factor

TEQ toxic equivalent

4 Principle

4.1 Spiking and extraction

Internal standards, analogues of the 2,3,7,8-substituted PCDDs/PCDFs labelled with a stable isotope (see Table 1) in a suitable solvent such as acetone, are spiked into a 1 l aqueous sample containing less than 1 % by mass solids. A minimum of one labelled standard per homologue group is used and the sample is extracted by one of two procedures as specified in 4.1 a) or 4.1 b).

a) Samples containing no visible particles are extracted with dichloromethane in a separatory funnel or by solid-phase extraction. The extract is concentrated for clean-up.

b) Samples containing visible particles are vacuum filtered through a glass-fibre filter. The filter is extracted in a Soxhlet extractor using toluene and the filtrate is extracted with dichloromethane in a separatory funnel. The dichloromethane extract is concentrated and combined with the Soxhlet extract prior to clean-up.

Other solvents and extraction techniques may be substituted, provided that all the performance criteria can be met.

4.2 Clean-up

After extraction, sample extracts are cleaned up to remove interfering components. Sample clean-ups may include back-extraction with acid and/or base, and gel-permeation, alumina, silica, Florisil[1)] or activated-carbon chromatography.

4.3 Concentration

After clean-up, the extract is concentrated to near dryness. Prior to injection, recovery standards are added to each extract, and an aliquot of the extract is injected into the gas chromatograph. The analytes are separated by the GC and detected by a high-resolution mass spectrometer. Two exact masses are monitored for each analyte.

Resolution equal to or greater than or 10 000 is recommended. High-resolution gas chromatography/high-resolution mass spectrometry at a resolution equal to or greater than 10 000 is, at present, required to achieve adequate sensitivity and selectivity, and to allow the use of all $^{13}C_{12}$-labelled standards. Resolution in the range of 6 000 to 10 000 should be acceptable if the absence of interferences has been documented. If a determination of PCDD/PCDF homologue group totals is required, then a resolution of 10 000 is necessary. At resolutions less than 10 000, some $^{13}C_{12}$-PCDFs interfere with native PCDDs of the same level of chlorination.

1) Florisil is an example of a suitable product available commercially.This information is given for the convenience of users of this International Standard and does not constitute an endorsement by ISO of this product.

Table 1 — PCDDs and PCDFs analyzed by this method

PCDDs/PCDFs	CAS registry	Labelled analogue	CAS registry
2,3,7,8-TCDD	1746-01-6	$^{13}C_{12}$-2,3,7,8-TCDD	76523-40-5
–	–	$^{13}C_{12}$-1,2,3,4-TCDD	–
Total TCDD	41903-57-5	–	–
2,3,7,8-TCDF	51207-31-9	$^{13}C_{12}$-2,3,7,8-TCDF	89059-46-1
Total TCDF	55722-27-5	–	–
1,2,3,7,8-PeCDD	40321-76-4	$^{13}C_{12}$-1,2,3,7,8-PeCDD	109719-79-1
Total PeCDD	36088-22-9	–	–
1,2,3,7,8-PeCDF	57117-41-6	$^{13}C_{12}$-1,2,3,7,8-PeCDF	109719-77-9
2,3,4,7,8-PeCDF	57117-31-4	$^{13}C_{12}$-2,3,4,7,8-PeCDF	116843-02-8
Total PeCDF	30402-15-4	–	–
1,2,3,4,7,8-HxCDD	39227-28-6	$^{13}C_{12}$-1 2,3,4,7,8-HxCDD	109719-80-4
1,2,3,6,7,8-HxCDD	57653-85-7	$^{13}C_{12}$-1,2,3,6,7,8-HxCDD	109719-81-5
1,2,3,7,8,9-HxCDD	19408-74-3	$^{13}C_{12}$-1,2,3,7,8,9-HxCDD	109719-82-6
Total HxCDD	34465-46-8	–	–
1,2,3,4,7,8-HxCDF	70648-26-9	$^{13}C_{12}$-1,2,3,4,7,8-HxCDF	114423-98-2
1,2,3,6,7,8-HxCDF	57117-44-9	$^{13}C_{12}$-1,2,3,6,7,8-HxCDF	116843-03-9
1,2,3,7,8,9-HxCDF	72918-21-9	$^{13}C_{12}$-1,2,3,7,8,9-HxCDF	116843-04-0
2,3,4,6,7,8-HxCDF	60851-34-5	$^{13}C_{12}$-2,3,4,6,7,8-HxCDF	116843-05-1
Total HxCDF	55684-94-1	–	–
1,2,3,4,6,7,8-HpCDD	35822-46-9	$^{13}C_{12}$-1,2,3,4,6,7,8-HpCDD	109719-83-7
Total HpCDD	37871-00-4	–	–
1,2,3,4,6,7,8-HpCDF	67562-39-4	$^{13}C_{12}$-1,2,3,4,6,7,8-HpCDF	109719-84-8
1,2,3,4,7,8,9-HpCDF	55673-89-7	$^{13}C_{12}$-1,2,3,4,7,8,9-HpCDF	109719-94-0
Total HpCDF	38998-75-3	–	–
OCDD	3268-87-9	$^{13}C_{12}$-OCDD	114423-97-1
OCDF	39001-02-0	$^{13}C_{12}$-OCDF	109719-78-0

4.4 Identification

An individual PCDD/PCDF is identified by comparing the GC retention time and the ion-abundance ratio of the two exact masses monitored with the respective retention time of an authentic standard and the theoretical or analytical ion-abundance ratio of the two exact masses.

The non-2,3,7,8-substituted isomers and congeners are identified by the agreement of their retention times and ion-abundance ratios with accepted values within predefined limits.

4.5 Quantification

Quantitative analysis is performed using selected-ion monitoring (SIM) in one of three ways.

a) For the 2,3,7,8-substituted PCDDs/PCDFs for which labelled analogues have been added to the sample (4.1), the isotope-dilution technique is used to calibrate the GC/MS system and to determine the concentration of each compound.

b) For the 2,3,7,8-substituted PCDDs/PCDFs for which labelled analogues are not added to the samples prior to extraction and for the labelled internal standards themselves, the internal-standard technique is used to calibrate the GC/MS system and to determine the concentration of each compound.

c) For non-2,3,7,8-substituted isomers and for all isomers at a given level of chlorination (i.e. total TCDDs), concentrations are determined using response factors from the calibration of the PCDDs/PCDFs at the same level of chlorination.

4.6 Analytical quality

The quality of the analysis is assured through reproducible calibration and testing of the procedures for extraction, clean-up, and GC/MS operation.

5 Contamination and interferences

5.1 Where possible, purify reagents by extraction or solvent rinse.

Solvents, reagents, glassware, and other sample processing hardware can yield artefacts and/or elevated baselines causing misinterpretation of chromatograms. Specific selection of reagents and purification of solvents by distillation in all-glass systems may be required.

5.2 Clean glassware such that the method blank requirements of this International Standard are met (9.4.3). An example of a cleaning procedure is given in 5.2 a) to 5.2 c).

a) Disassemble glassware with removable parts, particularly separatory funnels with fluoropolymer stopcocks, prior to washing with detergent. Rinse glassware with solvent and wash with a detergent solution as soon after use as is practical. Sonication of glassware in a detergent solution for approximately 30 s may aid in cleaning.

b) After washing with detergent, rinse glassware immediately, first with methanol, then with hot tap water. The tap water rinse shall be followed by another methanol rinse, then acetone, and then dichloromethane.

c) Immediately prior to use, pre-extract the Soxhlet apparatus with toluene for approximately 3 h. Shake separatory funnels with a dichloromethane/toluene mixture (80/20 by volume) for 2 min, drain, and then shake with pure dichloromethane for 2 min.

Proper cleaning of glassware is extremely important, because glassware not only can contaminate the samples but also can remove the analytes of interest by adsorption on the glass surface.

5.3 Demonstrate that all materials used in the analysis are free from interferences by running reference-matrix method blanks initially and with each sample batch (samples, up to a maximum of 20, processed through the extraction procedure on a given 12-h shift).

5.4 The reference matrix shall simulate, as closely as possible, the sample matrix under test. Ideally, the reference matrix shall not contain the PCDDs/PCDFs in detectable amounts, but shall contain potential interferents in the concentrations expected to be found in the samples to be analyzed.

Table 2 — Suggested quantitation relationships for individual PCDDs/PCDFs

PCDDs/PCDFs	Reference for retention time and quantitation	Relative retention time[a]	Minimum level[a,b] in water pg/l	Minimum level[a,b] in extract pg/µl
2,3,7,8-TCDF	$^{13}C_{12}$-2,3,7,8-TCDF	0,999 to 1,003	10	0,5
2,3,7,8-TCDD	$^{13}C_{12}$-2,3,7,8-TCDD	0,999 to 1,002	10	0,5
1,2,3,7,8-PeCDF	$^{13}C_{12}$-1,2,3,7,8-PeCDF	0,999 to 1,002	50	2,5
2,3,4,7,8-PeCDF	$^{13}C_{12}$-2,3,4,7,8-PeCDF	0,999 to 1,002	50	2,5
1,2,3,7,8-PeCDD	$^{13}C_{12}$-1,2,3,7,8-PeCDD	0,999 to 1,002	50	2,5
$^{13}C_{12}$-2,3,7,8-TCDF	$^{13}C_{12}$-1,2,3,4-TCDD	0,923 to 1,103	50	2,5
$^{13}C_{12}$-2,3,7,8-TCDD	$^{13}C_{12}$-1,2,3,4-TCDD	0,976 to 1,043	50	2,5
$^{13}C_{12}$-1,2,3,7,8-PeCDF	$^{13}C_{12}$-1,2,3,4-TCDD	1,000 to 1,425	50	2,5
$^{13}C_{12}$-2,3,4,7,8-PeCDF	$^{13}C_{12}$-1,2,3,4-TCDD	1,011 to 1,526	50	2,5
$^{13}C_{12}$-1,2,3,7,8-PeCDD	$^{13}C_{12}$-1,2,3,4-TCDD	1,000 to 1,567	50	2,5
1,2,3,4,7,8-HxCDF	$^{13}C_{12}$-1,2,3,4,7,8-HxCDF	0,999 to 1,001	50	2,5
1,2,3,6,7,8-HxCDF	$^{13}C_{12}$-1,2,3,6,7,8-HxCDF	0,997 to 1,005	50	2,5
1,2,3,7,8,9-HxCDF	$^{13}C_{12}$-1,2,3,7,8,9-HxCDF	0,999 to 1,001	50	2,5
2,3,4,6,7,8-HxCDF	$^{13}C_{12}$-2,3,4,6,7,8-HxCDF	0,999 to 1,001	50	2,5
1,2,3,4,7,8-HxCDD	$^{13}C_{12}$-1,2,3,4,7,8-HxCDD	0,999 to 1,001	50	2,5
1,2,3,6,7,8-HxCDD	$^{13}C_{12}$-1,2,3,6,7,8-HxCDD	0,998 to 1,004	50	2,5
1,2,3,7,8,9-HxCDD	See note[c]	1,000 to 1,019	50	2,5
1,2,3,4,6,7,8-HpCDF	$^{13}C_{12}$-1,2,3,4,6,7,8-HpCDF	0,999 to 1,001	50	2,5
1,2,3,4,7,8,9-HpCDF	$^{13}C_{12}$-1,2,3,4,7,8,9-HpCDF	0,999 to 1,001	50	2,5
1,2,3,4,6,7,8-HpCDD	$^{13}C_{12}$-1,2,3,4,6,7,8-HpCDD	0,999 to 1,001	50	2,5
OCDD	$^{13}C_{12}$-OCDD	0,999 to 1,001	100	5,0
OCDF	$^{13}C_{12}$-OCDD	0,999 to 1,008	100	5,0
$^{13}C_{12}$-1,2,3,4,7,8-HxCDF	$^{13}C_{12}$-1,2,3,7,8,9-HxCDD	0,944 to 0,970	—	—
$^{13}C_{12}$-1,2,3,6,7,8-HxCDF	$^{13}C_{12}$-1,2,3,7,8,9-HxCDD	0,949 to 0,975	—	—
$^{13}C_{12}$-1,2,3,7,8,9-HxCDF	$^{13}C_{12}$-1,2,3,7,8,9-HxCDD	0,977 to 1,047	—	—
$^{13}C_{12}$-2,3,4,6,7,8-HxCDF	$^{13}C_{12}$-1,2,3,7,8,9-HxCDD	0,959 to 1,021	—	—
$^{13}C_{12}$-1,2,3,4,7,8-HxCDD	$^{13}C_{12}$-1,2,3,7,8,9-HxCDD	0,977 to 1,000	—	—
$^{13}C_{12}$-1,2,3,6,7,8-HxCDD	$^{13}C_{12}$-1,2,3,7,8,9-HxCDD	0,981 to 1,003	—	—
$^{13}C_{12}$-1,2,3,4,6,7,8-HpCDF	$^{13}C_{12}$-1,2,3,7,8,9-HxCDD	1,043 to 1,085	—	—
$^{13}C_{12}$-1,2,3,4,7,8,9-HpCDF	$^{13}C_{12}$-1,2,3,7,8,9-HxCDD	1,057 to 1,151	—	—
$^{13}C_{12}$-1,2,3,4,6,7,8-HpCDD	$^{13}C_{12}$-1,2,3,7,8,9-HxCDD	1,086 to 1,110	—	—
$^{13}C_{12}$-OCDD	$^{13}C_{12}$-1,2,3,7,8,9-HxCDD	1,032 to 1,311	—	—

[a] Minimum levels and relative retention times are given for guidance only.

[b] The minimum level (ML) for each analyte is defined as the level for which the entire analytical system shall give a recognizable signal and acceptable calibration point. It is equivalent to the concentration of the lowest calibration standard, assuming that all method-specific sample masses, volumes and clean-up procedures have been used, i.e. based on 1 l of sample.

[c] The retention time reference for 1,2,3,7,8,9-HxCDD is $^{13}C_{12}$-1,2,3,6,7,8-HxCDD; 1,2,3,7,8,9-HxCDD is quantified using the averaged responses for $^{13}C_{12}$-1,2,3,4,7,8-HxCDD and $^{13}C_{12}$-1,2,3,6,7,8-HxCDD.

Interfering compounds in the sample extracts can vary considerably from source to source, depending on the diversity of the site being sampled. These compounds can be present at concentrations several orders of magnitude higher than the target PCDDs/PCDFs. The most frequently encountered interferences are chlorinated biphenyls, methoxybiphenyls, hydroxydiphenyl ethers, benzylphenyl ethers, polynuclear aromatics, and pesticides. Because this International Standard applies to very low levels of PCDDs/PCDFs, the elimination of interferences is essential. The example clean-ups given in Clause 13 can be used to reduce or eliminate these interferences and thereby permit reliable determination of the PCDDs/PCDFs at the concentrations shown in Table 2.

5.5 When a reference matrix that simulates the sample matrix under test is not available, use reagent water (6.1) as a substitute.

5.6 Number each piece of reusable glassware to associate that glassware with the processing of a particular sample. This will assist the laboratory in tracking possible sources of contamination for individual samples, identifying glassware associated with highly contaminated samples that may require extra cleaning, and determining when glassware shall be discarded.

6 Reagents and standards

Use only reagents of recognized analytical grade, unless otherwise specified.

6.1 **Water**, complying with grade 3 as defined in ISO 3696.

6.2 pH adjustment and back-extraction procedures.

6.2.1 **Potassium hydroxide solution**.

Dissolve 20 g of potassium hydroxide, KOH, in 100 ml of water.

6.2.2 **Sulfuric acid**, H_2SO_4, ρ = 1,84 g/ml.

6.2.3 **Hydrochloric acid**, c(HCl) = 6 mol/l.

6.2.4 **Sodium chloride solution**.

Dissolve 5 g of sodium chloride, NaCl, in 100 ml of water.

6.3 Solution drying and evaporation procedures.

6.3.1 **Sodium sulfate**, Na_2SO_4, granular, anhydrous.

Rinse granular, anhydrous sodium sulfate with dichloromethane (20 ml/g), heat at 400 °C for at least 1 h, cool in a desiccator, and store in a pre-cleaned glass bottle with a hermetically sealing screw-cap.

If, during heating, the sodium sulfate develops a noticeable greyish cast (due to the presence of carbon in the crystal matrix), discard, as it is not suitable for use. Extraction (in lieu of simple rinsing) with dichloromethane and heating at a lower temperature can produce sodium sulfate that is suitable for use.

6.3.2 **Nitrogen**, N_2 99,999 %.

6.4 **Extraction solvents**

The extraction solvents, distilled in glass, of pesticide quality and certified to be free of interferences, include the following:

a) **Acetone**, C_3H_6O.

b) **Toluene**, C_7H_8.

c) **Cyclohexane**, C_6H_{12}.

d) **Hexane**, C_6H_{14}.

e) **Methanol**, CH_3OH.

f) **Dichloromethane**, CH_2Cl_2.

g) **Nonane,** C_9H_{20}.

6.5 GPC calibration solution, dichloromethane containing 300 mg/ml of corn oil; 15 mg/ml of bis(2-ethylhexyl)phthalate, $C_{24}H_{38}O_4$; 1,4 mg/ml of pentachlorophenol, C_6Cl_5OH; 0,1 mg/ml of perylene, $C_{20}H_{12}$; and 0,5 mg/ml of sulfur, S.

6.6 Adsorbents for sample clean-up.

6.6.1 Silica

6.6.1.1 Activated silica, 75 to 140 µm.

Rinse silica with dichloromethane, heat at 180 °C for at least 1 h, cool in a desiccator, and store in a pre-cleaned glass bottle with a hermitically sealing screwcap.

6.6.1.2 Acid silica, 30 % mass fraction.

Thoroughly mix 44,0 g of concentrated sulfuric acid (6.2.2) with 100 g of activated silica in a clean container. Break up aggregates with a stirring rod until a uniform mixture is obtained. Store in a bottle with a fluoropolymer-lined screw-cap.

6.6.1.3 Basic silica.

Thoroughly mix 30 g of sodium hydroxide solution [c(NaOH) = 1 mol/l] with 100 g of activated silica in a clean container. Break up aggregates with a stirring rod until a uniform mixture is obtained. Store in a bottle with a fluoropolymer-lined screw cap.

6.6.1.4 Potassium silicate.

Dissolve 56 g of high-purity potassium hydroxide (KOH) in 300 ml of methanol in a 750 ml to 1 000 ml flat-bottom flask. Add 100 g of silica and a stirring bar, and stir on a hotplate at 60 °C to 70 °C for 1 h to 2 h. Decant the liquid and rinse the potassium silicate twice with 100-ml portions of methanol, followed by a single rinse with 100 ml of dichloromethane. Spread the potassium silicate on solvent-rinsed aluminium foil and dry for 2 h to 4 h in a hood. Activate the potassium silicate overnight at 200 °C to 250 °C.

6.6.2 Alumina

One of two types of alumina, acid or basic, may be used in the clean-up of sample extracts, provided that the laboratory meet the performance specifications for the recovery of internal standards in accordance with 9.3. The same type of alumina shall be used for all samples, including those used to demonstrate initial precision and recovery (9.2).

a) **Acid alumina**, activated by heating at 130 °C for at least 12 h.

b) **Basic alumina**, activated by heating at 600 °C for at least 24 h.

Store at 130 °C in a covered flask. Use within 5 d of activating.