
Kakovost vode - Določevanje tributilkositra (TBT) v celotnem vzorcu vode z ekstrakcijo na trdni fazi (SPE) s plinsko kromatografijo in s trojno kvadropolno masno spektrometrijo

Water quality - Determination of tributyl tin (TBT) in whole water samples using solid phase extraction (SPE) and gas chromatography with triple quadrupole mass spectrometry

Wasserbeschaffenheit - Bestimmung von Tributylzinn (TBT) in Gesamtwasserproben mittels Festphasenextraktion (SPE) und Gaschromatographie mit Triple-Quadrupol-Massenspektrometrie

Qualité de l'eau - Dosage du tributylétain (TBT) dans des échantillons d'eau totale par extraction sur phase solide (SPE) et chromatographie en phase gazeuse avec spectrométrie de masse triple quadrupôle

Ta slovenski standard je istoveten z: CEN/TS 16692:2015

ICS:

13.060.50	Preiskava vode na kemične snovi	Examination of water for chemical substances
71.040.50	Fizikalnokemijske analitske metode	Physicochemical methods of analysis

SIST-TS CEN/TS 16692:2015**en,fr,de**

iTeh STANDARD PREVIEW
(standards.iteh.ai)

[SIST-TS CEN/TS 16692:2015](https://standards.iteh.ai/catalog/standards/sist/4c3a9452-6adb-4d33-b3f8-39cf0bc266e5/sist-ts-cen-ts-16692-2015)

<https://standards.iteh.ai/catalog/standards/sist/4c3a9452-6adb-4d33-b3f8-39cf0bc266e5/sist-ts-cen-ts-16692-2015>

TECHNICAL SPECIFICATION
SPÉCIFICATION TECHNIQUE
TECHNISCHE SPEZIFIKATION

CEN/TS 16692

April 2015

ICS 13.060.50

English Version

Water quality - Determination of tributyltin (TBT) in whole water samples - Method using solid phase extraction (SPE) with SPE disks and gas chromatography with triple quadrupole mass spectrometry

Qualité de l'eau - Dosage du tributylétain (TBT) dans la totalité des échantillons d'eau - Méthode par extraction sur phase solide (SPE) avec disques SPE et chromatographie en phase gazeuse avec spectrométrie de masse triple quadrupôle

Wasserbeschaffenheit - Bestimmung von Tributylzinn (TBT) in Gesamtwasserproben - Verfahren mittels Festphasenextraktion (SPE) mit SPE-Disks und Gaschromatographie mit Triple-Quadrupole Massenspektrometrie

This Technical Specification (CEN/TS) was approved by CEN on 1 April 2014 for provisional application.

The period of validity of this CEN/TS is limited initially to three years. After two years the members of CEN will be requested to submit their comments, particularly on the question whether the CEN/TS can be converted into a European Standard.

CEN members are required to announce the existence of this CEN/TS in the same way as for an EN and to make the CEN/TS available promptly at national level in an appropriate form. It is permissible to keep conflicting national standards in force (in parallel to the CEN/TS) until the final decision about the possible conversion of the CEN/TS into an EN is reached.

CEN members are the national standards bodies of Austria, Belgium, Bulgaria, Croatia, Cyprus, Czech Republic, Denmark, Estonia, Finland, Former Yugoslav Republic of Macedonia, France, Germany, Greece, Hungary, Iceland, Ireland, Italy, Latvia, Lithuania, Luxembourg, Malta, Netherlands, Norway, Poland, Portugal, Romania, Slovakia, Slovenia, Spain, Sweden, Switzerland, Turkey and United Kingdom.



EUROPEAN COMMITTEE FOR STANDARDIZATION
COMITÉ EUROPÉEN DE NORMALISATION
EUROPÄISCHES KOMITEE FÜR NORMUNG

CEN-CENELEC Management Centre: Avenue Marnix 17, B-1000 Brussels

Contents

	Page
Foreword.....	3
Introduction	4
1 Scope	5
2 Normative references	5
3 Principle.....	5
4 Interferences	5
5 Reagents.....	6
6 Apparatus	8
7 Sampling.....	9
8 Procedure	9
8.1 Sample preparation	9
8.2 Derivatization	9
8.2.1 General.....	9
8.2.2 Derivatization procedure.....	10
8.3 Extraction with SPE-disks	10
8.4 Clean-up of the extract.....	11
8.5 Solvent concentration step.....	11
8.6 Gas chromatograph.....	11
8.7 Identification of individual compounds by GC-MS	11
8.8 Blank value measurements	12
9 Calibration	12
9.1 General requirements.....	12
9.2 Calibration of the GC-step	13
9.3 Calibration of the total procedure using the internal standard	14
9.4 Determination of procedural recovery values	15
9.5 Determination of derivatization standard recovery.....	15
10 Calculation.....	16
11 Expression of results	17
12 Test report	17
Annex A (informative) Suitable gas chromatographic conditions and example chromatograms	18
Annex B (informative) Repeatability and reproducibility data.....	20
Annex C (informative) Example of conditions for automated solid-phase extraction	21
Annex D (informative) Silica clean-up	22
D.1 Silica for the clean-up column.....	22
D.2 Clean-up column.....	22
D.3 Eluent for cleaning extract.....	22
D.4 Clean-up of extract	22
Bibliography	23

Foreword

This document (CEN/TS 16692:2015) has been prepared by Technical Committee CEN/TC 230 "Water analysis", the secretariat of which is held by DIN.

Attention is drawn to the possibility that some of the elements of this document may be the subject of patent rights. CEN [and/or CENELEC] shall not be held responsible for identifying any or all such patent rights.

This document has been prepared under a mandate given to CEN by the European Commission and the European Free Trade Association, and supports essential requirements of the Water Framework Directive (WFD, 2000/60/EC), and the Directive on Environmental Quality Standards (Directive 2008/105/EC).

According to the CEN-CENELEC Internal Regulations, the national standards organizations of the following countries are bound to announce this Technical Specification: Austria, Belgium, Bulgaria, Croatia, Cyprus, Czech Republic, Denmark, Estonia, Finland, Former Yugoslav Republic of Macedonia, France, Germany, Greece, Hungary, Iceland, Ireland, Italy, Latvia, Lithuania, Luxembourg, Malta, Netherlands, Norway, Poland, Portugal, Romania, Slovakia, Slovenia, Spain, Sweden, Switzerland, Turkey and the United Kingdom.

WARNING — Persons using this Technical Specification should be familiar with usual laboratory practice. This Technical Specification 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.

IMPORTANT — It is absolutely essential that tests conducted according to this Technical Specification be carried out by suitably trained staff.

STANDARD PREVIEW
(standards.iteh.ai)
<https://standards.iteh.ai/catalog/standards/sist/4c3a9452-6adb-4d33-b3f8-39cf0bc266e5/sist-ts-cen-ts-16692-2015>

Introduction

Tributyltin (TBT) is a priority substance listed in Annex X of the EU Water Framework Directive (WFD, Directive 2000/60/EC) for which Environmental Quality Standards (EQS) have been set at EU level for inland as well as other surface waters to protect the aquatic environment against chemical pollution (Directive 2008/105/EC). With the exception of metals, the EQSs are expressed as total concentrations in the whole water sample. Furthermore, analytical methods used in WFD monitoring need to meet certain requirements as regards the minimum limit of quantification and the maximum tolerable measurement uncertainty (Directive 2009/90/EC). So far, there is no standardized method available for the determination of TBT in whole water samples fulfilling those requirements. Hence, the European Commission mandated CEN to develop or improve standards in support of the implementation of the monitoring requirements of WFD.

Directive 2008/105/EC has been amended by Directive 2013/39/EU, however this standard has been developed for the analysis of TBT as listed in Annex A of Directive 2008/105/EC.

The annual average environmental quality standard (AA-EQS) value for TBT is 0,0002 µg/l and is defined for the concentration in the whole water sample, including suspended particulate matter (SPM) present in the sample. As compounds like TBT, sorb strongly to environmental solids, the fraction bound to particles may be substantial. Therefore it is important to be able to handle whole water samples within the analytical process. Identification and quantification of TBT at trace level concentrations often require both high sensitive chromatographic equipment and effective enrichment steps.

iTeh STANDARD PREVIEW (standards.iteh.ai)

[SIST-TS CEN/TS 16692:2015](https://standards.iteh.ai/catalog/standards/sist/4c3a9452-6adb-4d33-b3f8-39cf0bc266e5/sist-ts-cen-ts-16692-2015)

<https://standards.iteh.ai/catalog/standards/sist/4c3a9452-6adb-4d33-b3f8-39cf0bc266e5/sist-ts-cen-ts-16692-2015>

1 Scope

This Technical Specification specifies a method for the determination of tributyltin cation (TBT) in whole water samples. It is applicable to the analysis of TBT in surface water, which may contain suspended particulate matter (SPM) up to 500 mg/l (whole water samples), groundwater, drinking water and seawater. The working range is 0,04 ng/l to 20 ng/l. The LOQ will be mainly determined by the blank value obtained during validation of this method.

NOTE 1 The method has been successfully applied to seawater samples during method development, but sea water samples were not included in the interlaboratory comparison.

NOTE 2 In this document TBT is synonymous for tributyltin cation.

NOTE 3 Near the lower limit of the working range the measurement uncertainties may be higher.

2 Normative references

The following documents, in whole or in part, are normatively referenced in this document and are indispensable for its application. For dated references, only the edition cited applies. For undated references, the latest edition of the referenced document (including any amendments) applies.

EN ISO 3696, *Water for analytical laboratory use - Specification and test methods (ISO 3696)*

EN ISO 5667-3, *Water quality - Sampling - Part 3: Preservation and handling of water samples (ISO 5667-3)*

3 Principle

TBT in the whole water sample is derivatized while stirring thoroughly. The derivatized target analyte is extracted using solid phase extraction with SPE disks, and subsequently concentrated by evaporation. An aliquot of the extract is brought on the gas chromatograph with programmed temperature vaporizing - large volume injection (PTV-LVI) and identified and quantified with a triple quadrupole mass spectrometric detection in single GC-MS reaction mode.

Water samples of 1 l are spiked with internal standards and brought to pH 4 to pH 5 with a sodium acetate buffer. Subsequently, TBT is ethylated by adding sodium tetra ethylborate (NaEt₄B) to the water samples, while rigorously stirring. Solid phase disk extraction is used for extracting ethylated TBT with mainly hexane as a solvent. The extract is then brought to pH 12 with sodium hydroxide [1]. The final extract is then concentrated to 300 µl. A volume of 20 µl is injected into the gas chromatograph using a PTV-LV injection technique followed by GC-MS/MS in single GC-MS reaction mode for separation and detection.

A deuterium-labelled TBT substance is used as internal standard for quantification of TBT. A TBT-spiking solution is used for the determination of procedural recovery values. A tri-alkylated spiking solution is used for checking the efficiency of the alkylation process and is added to each sample. Tetra-alkylated reference solutions are used for the calibration.

4 Interferences

The reagents can contain impurities of organotin compounds, including the derivatization reagent. It is absolutely essential to verify contamination before use by analysis of blanks. Glassware can become contaminated. Heat all used glassware to 450 °C, or clean the glassware with a 10 % (volume fraction) nitric acid solution before use, by decontamination overnight. Make sure the GC-system is not contaminated. Regularly refresh the wash solvents to ensure that no contamination occurs via the injection needle. Verify the GC-system before analysis by analysis of blank solvent.

Commercially available solid-phase extraction disks (SPE-disks) differ frequently in quality. Variations in the selectivity of the materials also frequently occur from batch to batch, thus possibly causing significant

CEN/TS 16692:2015 (E)

deviations in extraction yield. This does not basically impair their suitability, apart from a resulting higher detection limit of individual substances. To ensure that the measuring results show high trueness and precision, use materials of one batch for both measurement and calibration. Avoid major fluctuations in the extraction times and elution procedures within one sample sequence when analysing the samples. SPE - disks may be contaminated with mono-, di- or tributyltin cation compounds. Verify the contamination of the disks before use. Pre-cleaning can be achieved by pre-extracting the disks with a derivatization agent. To thoroughly clean magnetic stirrers, they can be shaken in a methanol-hexane solution (9:1, v/v) with 1 ml of 2 % derivatization agent. Decontaminate overnight and rinse three times with deionized water.

5 Reagents

The reagents shall be free from impurities possibly interfering with the GC-MS analysis.

Use solvents and reagents of sufficient purity, i.e. with negligibly low impurities compared with the concentration of analytes to be determined. As reagents use, as far as available “residual grade” or better in order to obtain low blanks. Verify by blank determinations and, if necessary, apply additional cleaning steps.

5.1 Water, Grade 1 according to EN ISO 3696.

5.2 Operating gases for the gas chromatography mass spectrometry, of high purity and in accordance with manufacturer's specifications.

5.3 Nitrogen of high purity, i.e. minimum 99,996 % by volume, for concentration by evaporation.

5.4 Solvents for extraction, chromatography and preparation of reference solutions.

- hexane, C₆H₁₄, (boiling point: 69 °C);
- *iso*-octane, C₈H₁₈ (boiling point: 99 °C);
- *iso*-propanol, C₃H₇OH (boiling point: 82 °C);
- methanol, CH₃OH (boiling point: 65 °C).

5.5 Acetate buffer solution, solution, $c(\text{CH}_3\text{COONa}) = 4 \text{ mol/l}$.

5.6 Sodium hydroxide, solution, $c(\text{NaOH}) = 10 \text{ mol/l}$.

5.7 Hydrochloric acid, $w(\text{HCl}) = 36 \text{ \% to } 38 \text{ \% mass fraction}$.

5.8 Nitric acid, $v(\text{HNO}_3) = 10 \text{ \% volume fraction}$.

5.9 Aluminium oxide, activated at 800 °C for 4 h, (10 ± 2) % deactivated.

5.10 Sodiumtetraethylborate, $w(\text{NaEt}_4\text{B}) = 2 \text{ \% mass fraction}$, (CAS Registry Number 15523-24-7).

5.11 Reference ethyl-TBT stock solution

This substance is used for the calibration. Use a commercially available solution, e. g. in *iso*-octane or the commercially available pure substance (Table 1). The stock solution is prepared by dissolving, e. g. 5 mg of the reference substance (precision of 0,001 mg) in 20 g of an appropriate solvent (precision of 0,01 g) e. g. hexane or *iso*-octane. Store stock solutions at temperatures between 1 °C and 5 °C, protected from light. Stock solutions with concentrations > 1 mg/g are stable for at least 12 months and at least 3 months for concentrations > 1 µg/g.

5.12 Reference TBT stock solution

This substance is used for spiking water samples for determination of procedural recovery values. Use a commercially available solution of TBT, e. g. TBT-chloride in *iso*-octane or the commercially available pure substance (Table 1). Stock solution is prepared as described in 5.11, with e. g. *iso*-propanol or methanol as solvent. Stock solutions with concentrations > 1 mg/g are stable for at least 12 months and at least 3 months for concentrations > 1 µg/g.

5.13 Derivatization standard stock solution

In order to check the efficiency of the derivatization process, choose a tri-alkylated cation substance not present in the sample with similar physicochemical properties as TBT, e. g. TPrT-Cl (Table 1). The ethyl derivative of the derivatization standard, e. g. ethyl-TPrT (Table 1) is used for calibration. Prepare stock solutions of the derivatization standard substances in the same way as specified for the reference stock solutions (5.11 and 5.12). Stock solutions with concentrations > 1 mg/g are stable for at least 12 months and at least 3 months for concentrations > 1 µg/g.

5.14 Internal standard solution

5.14.1 Internal standard for calculation of TBT concentration

As internal standard for quantification of TBT, a deuterium-labelled substance is used. The ethyl derivative is used in the calibration. In Table 1 internal standards are listed. Prepare stock solutions of the internal standard substances in the same way as specified for the reference stock solutions (5.11 and 5.12).

¹³C-enriched TBT might be used as an alternative internal standard, but suitability should be checked, as it has not been used in the method development nor in the interlaboratory comparison.

5.14.2 Internal standard for calculation of the derivatization standard

For calculation of the derivatization standard (5.13) concentration use, e. g. tetrapropyltin (Table 1) as internal standard or choose a substance with similar physicochemical properties as the derivatization standard (extraction behaviour, retention time). The internal standard should be tetra-alkylated. Prepare stock solutions of the internal standard substance in the same way as specified for reference stock solution (5.11).

5.15 Calibration working solutions

Use the ethyl derivative of TBT (5.11) and the derivatization standard (5.13) of a defined concentration, used for gas chromatography and suitable for the preparation of calibration solutions. Prepare a minimum of seven calibration solutions with concentrations according to the detection capability of the mass spectrometer. Combine and dilute internal standards (5.14) with hexane and *iso*-octane to produce solutions for the calibration range in a hexane - *iso*-octane (9:1, volume fraction) solvent. Store calibration solutions for maximum 3 days at temperatures between 1 °C and 5 °C protected from light.

5.16 TBT reference substance solution

Use TBT (5.12) of defined concentration, suitable for the preparation of a reference solution used for spiking water samples. Spike blank water samples for the determination of procedural recovery values (9.4).

5.17 Derivatization standard solution

Use the tri-alkylated derivatization standard (5.13) of defined concentration, suitable for the preparation of reference solutions used for spiking water samples. Spike each sample for calculation of the recovery (9.5).

CEN/TS 16692:2015 (E)

Table 1 — Reference substances, internal and derivatization standards and their ethyl-derivatives

Substance	Abbreviation	Molecular formula	Molar mass g/mol	EC number ^a	CAS RN ^b
Reference substance and ethyl derivative					
Tributyltin chloride (5.12)	TBT-Cl	C ₁₂ H ₂₇ SnCl	325,51	215–958–7	1461–22–9
Ethyltributyltin (5.11)	Ethyl-TBT	C ₁₄ H ₃₂ Sn	319,11	not applicable	19411–60–0
Deuterated internal standard and ethyl derivative (5.14.1)					
Tributyltin-d ₂₇ chloride	d ₂₇ -TBT-Cl	C ₁₂ D ₂₇ SnCl	352,51	not applicable	–
Ethyltributyltin-d ₂₇	Ethyl-d ₂₇ -TBT	C ₁₄ H ₅ D ₂₇ Sn	346,11	not applicable	–
Tetra-alkyltin standard (5.14.2)					
Tetrapropyltin	TePrT	C ₁₂ H ₂₈ Sn	291,05	218–536–0	2176–98–9
Derivatization standard and ethyl derivative (5.13)					
Tripropyltin chloride	TPrT-Cl	C ₉ H ₂₁ SnCl	283,41	218–910–3	2279–76–7
Ethyltripropyltin	Ethyl-TPrT	C ₁₁ H ₂₆ Sn	277,03	not applicable	3440–79–7
^a EC Number: European inventory of existing commercial substances (EINECS) or European list of notified chemical substances (ELINCS). ^b CAS RN: Chemical Abstracts Service Registry Number.					

SIST-TS CEN/TS 16692:2015

<https://standards.iteh.ai/catalog/standards/sist/4c3a9452-6adb-4d33-b3f8-39cf0bc266e5/sist-ts-cen-ts-16692-2015>

6 Apparatus

6.1 General

Equipment or parts of it which are likely to come into contact with the water sample or its extract shall be free from residues causing interferences. The use of vessels made of glass is recommended. Heat all glassware to 450 °C, or clean the glassware with 10 % (volume fraction) nitric acid solution. Decontaminate overnight and rinse three times with deionized water.

6.2 Sample flasks, e. g. brown glass, flat bottomed, with glass or PTFE coated stoppers, e. g. 250 ml or 500 ml and 1 000 ml.

6.3 Magnetic stirrer, including PTFE-coated magnetic stir bar of suitable size.

6.4 Drying ovens, capable of maintaining temperatures in the ranges of 100 °C to 800 °C for baking and storage of clean-up materials and maintaining temperatures up to 450 °C for baking glassware.

6.5 Solid-phase extraction disks (SPE disks), wide inner diameter: e. g. 45 mm, packed with an appropriate reversed phase adsorbent material, e. g. C₁₈-based or DVB-based adsorbent.

6.6 Vacuum device for solid-phase extraction, e. g. vacubox, extraction box or automated workstation for solid-phase extraction procedure capable for processing SPE-disks or automatic solid disk extractor, capable of extracting water samples up to 1 l with organic solvents and with automatic cleaning cycle.

6.7 Glass columns for chromatographic clean-up.

6.8 Evaporation device, based on nitrogen flow evaporation or rotary evaporator under reduced pressure.

6.9 Syringes, 10 µl, 25 µl, 50 µl, 100 µl, 1 000 µl, volume precision $\pm 2\%$.

6.10 Single volume pipettes, capacities between 100 µl and 50 ml.

6.11 Glass sample vials, dark coloured glass capacity e. g. 2 ml with 300 µl inserts, with inert cap and PTFE-coated septum.

6.12 Capillary gas chromatograph with a triple quadrupole mass spectrometer, (GC-MS/MS) using single GC-MS reaction mode, gas supply in accordance with the respective manufacturer's instructions.

6.13 Non-discriminating GC injector, e. g. splitless mode of a split or splitless injection system and programmable temperature vaporiser (PTV), programmable for large volume injection (LVI).

6.14 Automatic sampler with option for large volume injection (LVI), including syringes for normal injection (e. g. 1 µl and 2 µl) and LVI (e. g. 50 µl and 100 µl).

6.15 Capillary column, for gas chromatography, fused silica column with non-polar low bleed separating phase (e. g. 5 % diphenyl 95 % dimethyl polysiloxane, length 20 m, inner diameter 0,18 mm and film thickness 0,18 µm).

6.16 Pasteur pipettes

6.17 pH indicator strips, for the appropriate pH-ranges.

7 Sampling

iTeh STANDARD PREVIEW

For sampling, use thoroughly cleaned flat bottomed glass flasks (6.2). Fill the bottles completely with the water to be examined. Samples should be brought to pH ($2 \pm 0,2$) with hydrochloric acid (5.7) within 24 h.

If extraction requires the sample flask to be included in the working process, it is recommended to fill the bottle to the shoulder (e.g. about 1 000 ml or 2 000 ml when using a 1 000-ml or 2 000-ml flat bottomed sample flask).

Treat and analyse the samples as soon as possible after sample collection as specified in EN ISO 5667-3. Store the samples at temperatures between 1 °C and 5 °C, protected from light.

NOTE It is best to carry out the extraction as soon as practicable to minimize potential adsorption effects to glass.

8 Procedure

8.1 Sample preparation

In general, samples are examined without pre-treatment, e. g. suspended particulate matter is not removed prior to analysis. Do not filter the sample.

Large particles (e. g. leaves, little branches) should be removed using a metal sieve (screening gap 1 mm).

Calculate the exact volume of the water sample by weighing the sample flask before extraction and after emptying.

8.2 Derivatization

8.2.1 General

Bring a magnetic stirring rod (6.3) in the sample container (6.2), e. g. 1 000 ml flat-bottomed flask.