



BSI Standards Publication

**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**

**National foreword**

This Published Document is the UK implementation of CEN/TS 16692:2015.

The UK participation in its preparation was entrusted to Technical Committee EH/3/2, Physical chemical and biochemical methods.

A list of organizations represented on this committee can be obtained on request to its secretary.

This publication does not purport to include all the necessary provisions of a contract. Users are responsible for its correct application.

© The British Standards Institution 2015. Published by BSI Standards Limited 2015

ISBN 978 0 580 84470 6

ICS 13.060.50

**Compliance with a British Standard cannot confer immunity from legal obligations.**

This Published Document was published under the authority of the Standards Policy and Strategy Committee on 30 April 2015.

**Amendments issued since publication**

Date	Text affected
------	---------------

---

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.**

## **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.

## 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 (NaEt<sub>4</sub>B) 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