PD CEN/TS 16692:2015

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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

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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

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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.

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

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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.

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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 ($NaEt_4B$) 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

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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, C_6H_{14}, (boiling point: 69 °C);

— *iso*-octane, C_8H_{18} (boiling point: 99 °C);

— *iso*-propanol, C_3H_7OH (boiling point: 82 °C);

— methanol, CH_3OH (boiling point: 65 °C).

5.5 Acetate buffer solution, solution, $c(CH_3COONa)$ = 4 mol/l.

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

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

5.8 Nitric acid, $v(HNO_3)$ = 10 % volume fraction.

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

5.10 Sodiumtetraethylborate, $w(NaEt_4B)$ = 2 % 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.

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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 ethylderivative 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 ethylderivative 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).

^{13}C-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).

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