SLOVENSKI STANDARD
kSIST-TS FprCEN/TS 17985:2023

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Gradbeni proizvodi - Ocenjevanje sproščanja nevarnih snovi - Metode določevanja N-nitrozaminov v vzorcih zraka, pridobljenih v skladu s standardom EN 16516

Construction Products - Assessment of release of dangerous substances - Methods for the determination of N-nitrosamines in air samples derived by EN 16516

Bauprodukte: Bewertung der Freisetzung gefährlicher Stoffe - Verfahren zur Bestimmung von N-Nitrosaminen in Luftproben, die nach EN 16516 gewonnen wurden

Produits de construction - Évaluation de l'émission de substances dangereuses - Méthodes de détermination des N-nitrosamines dans des échantillons d'air prélevés conformément à l'EN 16516

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91.100.01	Gradbeni materiali na splošno	Construction materials in general

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English Version

Construction Products - Assessment of release of dangerous substances - Methods for the determination of N-nitrosamines in air samples derived by EN 16516

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This draft Technical Specification is submitted to CEN members for Vote. It has been drawn up by the Technical Committee CEN/TC 351.

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Recipients of this draft are invited to submit, with their comments, notification of any relevant patent rights of which they are aware and to provide supporting documentation.

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

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European foreword

This document (FprCEN/TS 17985:2023) has been prepared by Technical Committee CEN/TC 351 “Construction products – Assessment of release of dangerous substances”, the secretariat of which is held by NEN.

This document is currently submitted to the Vote on TS.

This document has been prepared under a Standardization Request given to CEN by the European Commission and the European Free Trade Association.

Introduction

This document describes a test procedure for the determination of N-nitrosamines in air samples derived by EN 16516:2017+A1:2020 that is able to determine N-nitrosamines at a level of ≤ 0,2 µg/m³.

1 Scope

This document describes a test procedure for sampling, elution, detection, and quantification of N-nitrosamines in air samples derived from a test chamber according to EN 16516:2017+A1:2020. The following N-nitrosamines are covered:

— N-Nitrosodimethylamine, CAS No. 62-75-9,

— N-Nitrosomethylethylamine, CAS No. 10595-95-6,

— N-Nitrosodiethylamine, CAS No. 55-18-5,

— N-Nitrosodipropylamine, CAS No. 621-64-7,

— N-Nitrosodiisopropylamine, CAS No. 601-77-4,

— N-Nitrosodibutylamine, CAS No. 924-16-3,

— N-Nitrosopiperidine, CAS No. 100-75-4,

— N-Nitrosopyrrolidine, CAS No. 930-55-2 and

— N-Nitrosomorpholine, CAS No. 59-89-2.

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.

EN 16516:2017+A1:2020, *Construction products: Assessment of release of dangerous substances - Determination of emissions into indoor air*

3 Terms and definitions

For the purposes of this document, the terms and definitions given in EN 16516:2017+A1:2020 and the following apply.

ISO and IEC maintain terminology databases for use in standardization at the following addresses:

— ISO Online browsing platform: available at https://www.iso.org/obp/

— IEC Electropedia: available at https://www.electropedia.org/

3.1
internal standard
compound of known concentration added to a sample to facilitate the qualitative identification and/or quantitative determination of the sample components

[SOURCE: ISO 16000-6:2021, 3.10]

3.2
N-nitrosamine
substance characterised by the -N-N=O functional group, usually formed by the reaction of an amine with a nitrosating agent at acidic pH

Note 1 to entry: The reacting amines primarily are secondary amines.

Note 2 to entry: An example for a nitrosating agent is nitrite.

[SOURCE: EN 71-12:2016, 3.3]

4 Abbreviations

GC-TEA	Gas chromatography - thermal energy analysis
HPLC-MS/MS	High performance liquid chromatography - tandem mass spectrometry
LOD	Limit of detection
LOQ	Limit of quantification
NDBA	N-Nitrosodibutylamine
NDEA	N-Nitrosodiethylamine
NDiPA	N-Nitrosodiisopropylamine
NDMA	N-Nitrosodimethylamine
NDPA	N-Nitrosodipropylamine
NMEA	N-Nitrosomethylethylamine
NMOR	N-Nitrosomorpholine
NPIP	N-Nitrosopiperidine
NPYR	N-Nitrosopyrrolidine

5 Sampling of N-nitrosamines from test chamber air

N-Nitrosamines in air samples are collected on special cartridges and are analysed either by GC-TEA or HPLC-MS/MS.

Air samples shall be collected in duplicate. For this, N-nitrosamines from test chamber air shall be collected simultaneously (or immediately sequentially) on two samplers.

A measured volume of 100 l of air from the emission test chamber is drawn at a controlled flow rate (from 1,5 l/min to 2,0 l/min) through the sampler at specified times (as specified in EN 16516:2017+A1:2020) during the emission test. The vapour-phase N-nitrosamines present in the chamber air are trapped on the samplers as the air passes through. The sampler shall prevent the formation of N-nitrosamines from amines, usually by use of an inhibitor (Example: Thermosorb-N Air Sampling Cartridges from Ellutia). The loaded samplers may be stored or transported for a maximum of seven days at room temperature before elution for analysis.

To confirm the absence of the N-nitrosamines, an additional sampling is recommended 24 h after the start of the emission test due to the high volatility of the N-nitrosamines.

NOTE Materials containing vulcanising agents have a potential to form N-nitrosamines.

6 Preparation for subsequent analysis

6.1 General

The samplers are extracted in opposite direction of air sampling.

6.2 Elution for subsequent analysis with GC-TEA

The loaded samplers are placed in an upright position with the “air-in” side on top. 100 µl internal standard solution (see 7.1.2) are added with a syringe and left for 5 min. The sampler is turned around that the “air-out” side of sampling is up and a 2 ml-vial is placed under the “air-in” side of the tube. The sampler is eluted with 2 ml dichloromethane/methanol 3:1 mixture. The eluates are then analysed by GC-TEA as described in 7.1.2.

NOTE Approximately 1 ml of extract is received, internal standard method compensates for varying extract volume.

6.3 Elution for subsequent analysis with HPLC-MS/MS

The loaded samplers are eluted with 1,5 ml methanol and made up to 2 ml. After shaking, the eluates are left to settle for 5 min and then filtrated through a 0,2 µm membrane filter. The eluates are then analysed by HPLC-MS/MS as described in 7.1.3.

NOTE Crystallization is sometimes observed after elution, therefore it is advisable to leave the eluates for 10 min before filtration.

6.4 Storage of eluted samples

The eluates can be stored for at least 14 days in a refrigerator protected from light at a temperature below 4 °C without analyte losses. Tight-sealing vials are required to prevent the loss of the solvent.

7 Analysis and quantification

7.1 Analytical method of determination

7.1.1 General

The analytical step shall be carried out twofold for each eluate.

7.1.2 Calibration and analysis with GC-TEA

A calibration shall be carried out before analysis of samples.

Commercially available standard solutions (single or mixture) may be used for calibration. N-Nitroso-propylbutylamine (NPBA) is used as internal standard.

Examples of stock solutions:

— Analyte stock solution (1 µg/ml of each analyte): 100 µl of the commercially available standard solution (100 µg/ml in methanol) is filled-up in a 10 ml brown glass flask to the mark with a mixture of dichloromethane/methanol 3:1.

— NPBA stock solution (1 µg/ml): 1 ml of the commercially available standard solution (1000 µg/ml in methanol) is filled-up in a 10 ml brown glass flask to the mark with methanol. 100 µl of this solution is filled-up in a 10 ml brown glass flask to the mark with a mixture of dichloromethane/methanol 3:1.

The calibration solutions are prepared in 2 ml brown glass vials from the stock solutions according to Table 1.

Table 1 — Scheme for preparation of calibration solutions for GC-TEA

Calibration solution	Analyte stock solution [µl]	NPBA stock solution [µl]	Fill up volume [a] [µl]	Concentration analytes [ng/ml]	Concentration NPBA [ng/ml]
1	0	100	900	0	100
2	25	100	875	25	100
3	50	100	850	50	100
4	100	100	800	100	100
5	150	100	750	150	100
6	250	100	650	250	100
7	350	100	550	350	100
8	500	100	400	500	100

[a] A mixture of dichloromethane/methanol 3:1 is used.

Example conditions for GC-TEA analysis:

— GC-Column: CP WAX 52 CB, 30 m × 0,25 mm × 0,25 µm

— Carrier gas: Helium 5,0, flow rate 1,2 ml/min

— Injector: PTV (solvent vent mode)

— Temperature program PTV: hold at 39 °C for 0,05 min, increase temperature with 720 °C/min to 250 °C and hold for 10 min

— Volume of injection: 5 µl

— Temperature program: hold at 60 °C for 2 min, increase temperature with 20 °C/min to 150 °C and hold for 9 min, increase temperature with 30 °C/min to 220 °C and hold for 2 min

— TEA interface: 250 °C

— Pyrolysis oven: 500 °C

A chromatogram of a calibration solution is shown in Figure 1.

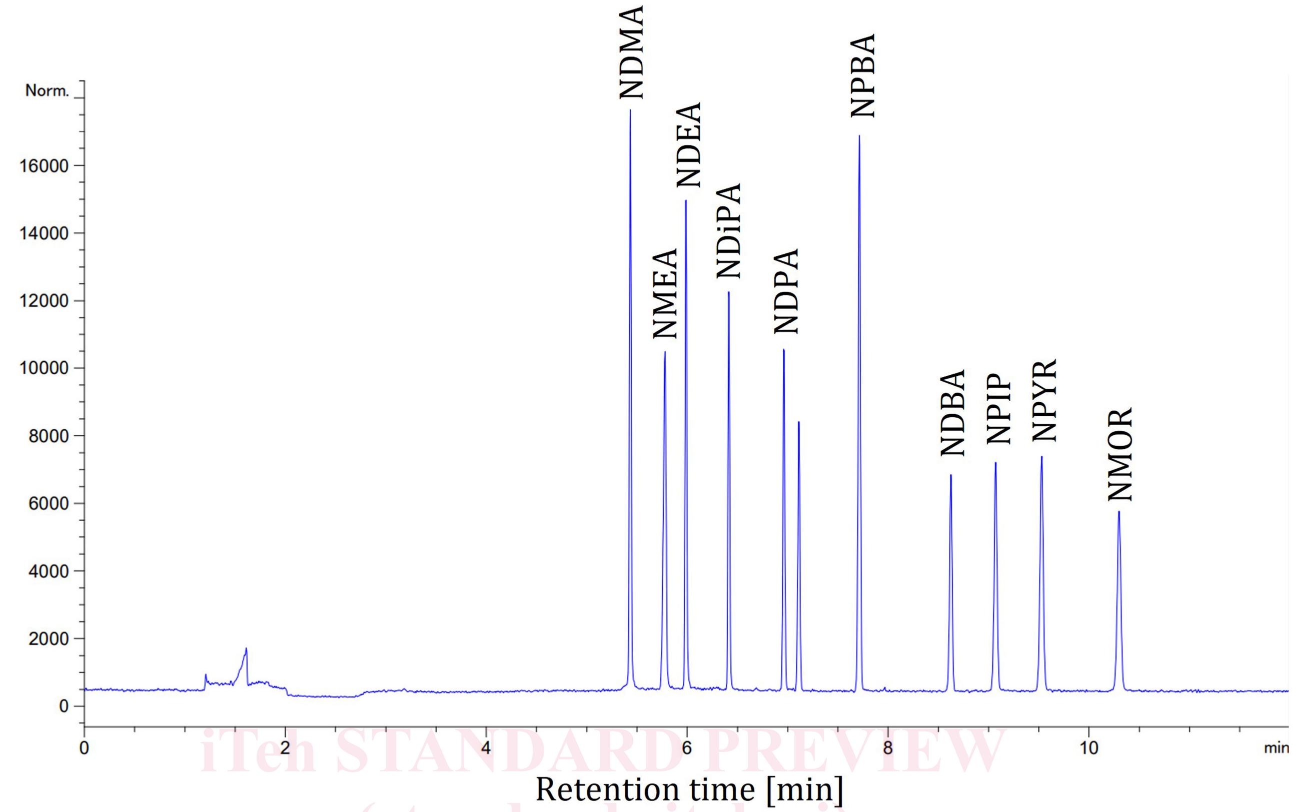

Figure 1 — Chromatogram of a calibration solution for analysis with GC-TEA

Chromatographic separation shall be sufficient to allow clear identification and quantification, especially separation between NDBA and NPIP.

Analytes and the internal standard are identified by retention times. Although a TEA operating in the nitrosamine modus is highly specific for N-Nitroso-compounds, the validity of a positive result is secured by either using a second column of different polarity or preferably by applying the following procedure.

As N-nitrosamines are not stable when exposed to UV-light, a part of the eluate is transferred to a UV-transparent vial. This vial is exposed to a UV-lamp with a wavelength of 365 nm for 3 h and measured again.

In case of a decrease in the original signal of more than half the original peak is confirmed as a N-nitrosamine. The degradation process can be controlled by the internal standard signal which should disappear nearly completely in the treated extract using the described procedure.

7.1.3 Calibration and analysis with HPLC-MS/MS

A calibration shall be carried out before analysis of samples.

The system is calibrated with a multi-component standard (e.g. a commercially available EPA 8270 appendix IX nitrosamine mix with concentrations of each 2000 µg/ml). N-Nitrosodiethylamin-D10 can be used as internal standard. Dilutions in methanol with the following concentrations are prepared in brown glass vials: 100 ng/ml; 50 ng/ml; 20 ng/ml; 10 ng/ml; 5 ng/ml; 2 ng/ml; 1 ng/ml. To calibrate, each standard solution is measured three times.