SLOVENSKI STANDARD
SIST-TS CEN/TS 18044:2024

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Zunanji zrak - Določanje koncentracije levoglukozana - Kromatografska metoda

Ambient air - Determination of the concentration of levoglucosan - Chromatographic method

Außenluft - Bestimmung der Konzentration von Levoglucosan - Chromatographisches Verfahren

Air ambiant - Détermination de la concentration de lévoglucosan - Méthode chromatographique

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TECHNICAL SPECIFICATION

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TECHNISCHE SPEZIFIKATION

CEN/TS 18044

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ICS 13.040.20

English Version

Ambient air - Determination of the concentration of levoglucosan - Chromatographic method

Air ambiant - Détermination de la concentration de lévoglucosan - Méthode chromatographique

Außenluft - Bestimmung der Konzentration von Levoglucosan - Chromatographisches Verfahren

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European foreword

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Introduction

Emissions from the combustion of biomass (e.g. wood firing) contribute to particulate air pollution (PM_{10}, $PM_{2,5}$). Under inversion weather conditions in winter, the contribution of biomass combustion to the particulate load can increase up to 50 % of the PM_{10} average daily value. As levoglucosan originates by pyrolysis of materials containing cellulose, it is a suitable tracer for biomass combustion [1 to 4].

The formation of levoglucosan from cellulose proceeds as follows: The cellulose polymer is thermally split into oligomers. Conformation change of β-D-glucose units, followed by dehydration leads to levoglucosan as shown in Figure 1.
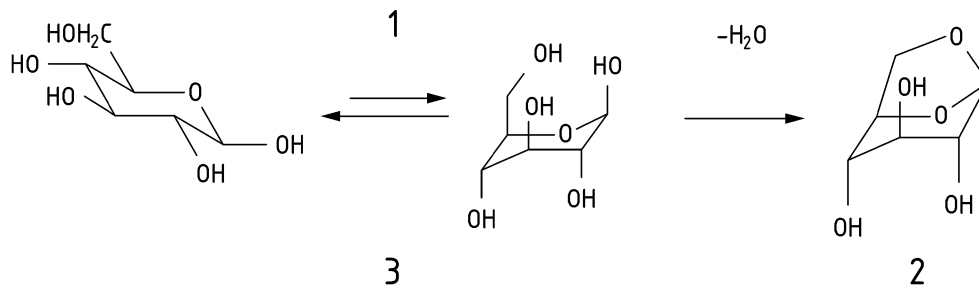
Key

1   Conformation change

2   Levoglucosan

3   β-D-Glucose

Figure 1 — Formation of levoglucosan from β-D-glucose

In a similar way, units of galactose and mannose, which also occur in hemicellulose, can be converted to galactosan and mannosan.

Laboratory-scale wood combustion studies and also estimates derived from ambient air measurements, can be used to estimate the contribution of biomass combustion to the fine particulate load on the basis of the levoglucosan concentration. Conversion factors of 8 to 20 were obtained for calculation of the PM_{10} concentration attributable to wood combustion from the levoglucosan concentration.

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1 Scope

This document specifies a chromatographic method for the determination of levoglucosan in aqueous or organic extracts of filter samples collected in accordance with EN 12341:2023 [5]. The method has been tested for concentrations of ca. 10 ng/m^3 up to ca. 3 000 ng/m^3 with a sampling duration of 24 h. The procedure is also suitable for the determination of galactosan and mannosan.

Depending on the analysis instrumentation used, the carbohydrates inositol, glycerol, threitol/erythritol, xylitol, arabitol, sorbitol, mannitol, threalose, mannose, glucose, galactose and fructose can also be determined. However, no performance characteristics are given for these compounds in this document.

2 Normative references

There are no normative references in this document.

3 Terms and definitions

For the purposes of this document, the following terms and definitions apply.

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

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

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

3.1
internal standard solution
solution of a known substance of known concentration, added to the sample before chromatographic analysis

[SOURCE: EN 15549:2008, 3.5 [6]]

3.2
surrogate standard solution
solution of a known substance and of known concentration, used to spike filters before extraction in order to check the recovery efficiency

[SOURCE: EN 15549:2008, 3.10]

4 Symbols and abbreviations

GC-MS   Gas Chromatography – Mass Spectrometry

HPLC-MS High Performance Liquid Chromatography – Mass Spectrometry

IC-PAD   Ion Chromatography – Pulsed Amperometric Detection

BSTFA   N,O-Bis(trimethylsilyl)trifluoroacetamide

5 Principle

Fine particulate samples are collected on filters in accordance with EN 12341:2023. Subsamples are extracted with water (for IC-PAD analysis) or with an organic solvent (e.g. methanol or methanol/dichloromethane mixtures, for GC-MS analysis). After a method-specific sample preparation the extract is analysed by IC-PAD or by GC-MS after silylation.

NOTE   Levoglucosan can also be analysed by HPLC-MS [7; 8; 9]. This method is not validated.

6 Equipment

6.1 Sampling

6.1.1 Sampling device

A particle sampler equipped with a particle selective sampling head (e.g. for PM_{10} and $PM_{2,5}$), a filter holder and a volume regulated pump. Appropriate sampler types are specified in EN 12341:2023. High volume samplers (sampling volume 700 m^3/d, filter diameter 150 mm) and low volume samplers (sampling volume 55 m^3/d, filter diameter 47 mm) may be used (see [5]).

6.1.2 Particle filter

Quartz fibre or glass fibre filter with a diameter suitable for the sampler with a separation efficiency of at least 99,5 % at an aerodynamic diameter of 0,3 µm.

6.2 Apparatus for sample preparation

The following apparatus is required:

— filter punch with support (optional);

— extractions vessels: e.g. conical polypropylene centrifuge tubes with leakproof caps (for IC-PAD); glass centrifuge tubes with PTFE caps (for GC-MS)

— accelerated solvent extraction apparatus, laboratory shaker, ultrasonic bath or Soxhlet extraction apparatus;

— centrifuge (optional);

— filtering equipment.

6.3 Analytical equipment

6.3.1 IC-PAD

Liquid chromatograph with:

— pump;

— autosampler (optional);

— vacuum degasser or eluants under N_2 bubbling;

— precolumn (optional);

— carbohydrate column;

— pulsed amperometric detector (with gold electrode).

6.3.2 GC-MS

GC-MS system with:

— autosampler (optional);

— split/splitless injection system;

— column: e.g. 95 % dimethyl-, 5 % diphenylpolysiloxane, 30 m length, 0,25 mm internal diameter, 0,25 µm film thickness;

— mass selective detector.

6.4 Chemicals and accessories

Pure substances (with CAS No.):

— levoglucosan (498-07-7).

Real samples can contain the following components; adequate chromatographic separation of levoglucosan from these components shall be ensured:

— D(–)-fructose (57-48-7);

— D(+)-glucose (50-99-7);

— mannosan (14168-65-1);

— galactosan (644-76-8).

The following components are suitable for checking the separation performance of the analytical column used, depending upon the chromatographic conditions:

— D(+)-arabitol (488-82-4) or L(–)-arabitol (7643-75-6);

— sedoheptulosan (469-90-9);

— mannosan (14168-65-1);

— D-mannitol (69-65-8).

Internal standard (required for GC-MS, optional for IC-PAD), e.g.:

— D-threitol (2418-52-2);

— methyl-ß-arabinopyranoside;

— sedoheptulosan.

The internal standard for GC-MS checks shall be silylated. Contact with protic solvents (water, methanol, etc.) shall be avoided.

Surrogate standard (required for GC-MS):

— deuterated or C13-labelled anhydrosugars (e.g. levoglucosan, sedoheptulosan);

— sedoheptulosan.

7 Sampling

Ambient air particles are collected on filters using the devices specified in 6.1.1. The samples may be stored at room temperature for a maximum of 3 weeks [7]. Cooled storage is recommended. For longer periods (up to 12 months) storage at ≤ –10 °C is required.

8 Sample preparation and analysis

8.1 General

Work-up and analysis differ depending on the chosen analysis method. In the following text, the work-up and analysis steps are described separately for the methods IC-PAD (see 8.2) and GC-MS (see 8.3). More detailed descriptions are given in Annex A and Annex B.

8.2 IC-PAD method

8.2.1 Sample preparation

The filter or an aliquot portion of its area is introduced into the extraction vessel and a defined volume of ultrapure water is added. Extraction is performed with the aid of a laboratory shaker or in an ultrasonic bath. The extract is centrifuged or filtered as required.

8.2.2 Eluent preparation

The eluent is prepared by mixing a carbonate-free 50 % sodium hydroxide solution with degassed ultrapure water. Chromatographic separation can be improved by addition of sodium acetate. The concentrations of NaOH and, if applicable, of sodium acetate for achieving optimum separation performance shall be determined experimentally.

The maximum permissible eluent concentrations depend upon the column. The manufacturer's instructions are to be observed. The retention time generally increases at low eluent concentrations. Low eluent concentrations can no longer displace carbonate ions from the column, leading more rapidly to a reduction of the column capacity. Too low an eluent concentration can also influence the electrochemical reaction at the gold electrode of the detector and lead to deposits.

The separation performance of a column contaminated by carbonate can be improved by conditioning with a more highly concentrated sodium hydroxide solution to which sodium acetate has been added.

It is necessary to ensure that no carbon dioxide from the ambient air is taken up by the sodium hydroxide solution during eluent preparation. Degassing under N_2 bubbling is a way to prevent this.

8.2.3 Analysis

The instrument is set up and operated according to the manufacturer's instructions.

An aliquot of the solution is analysed by IC-PAD. Application examples are given in Annex A.

8.2.4 Calibration

Prepare solutions of different concentrations of levoglucosan, mannosan and galactosan by dissolving the substances in water. The peak areas of the analytes shall show a linear relation with the amount of analyte added.

8.3 GC-MS method

8.3.1 Sample preparation

A known amount of surrogate standard solution is added to the filter or a filter piece, the filter is dried. The dried filter is extracted with methanol or a methanol/dichloromethane mixture, e.g. in an ultrasonic bath for 30 min in total (or by using ASE or Soxhlet extraction). The extract is evaporated to a small volume, transferred into a small vial and evaporated to complete dryness.

NOTE 1   Any moisture can interfere with the subsequent silylation reaction.

A silylation reagent is added, the vial is closed and kept at room temperature for e.g. two hours.

NOTE 2   The most common silylation reagent is a mixture of BSTFA and TMCS (trimethylchlorosilane) and/or pyridine. Acetone or other non-protic solvents can also be used.

Then a known amount of silylated internal standard solution is added to the extract before analysis.

8.3.2 Analysis

The instrument is set up and operated according to the manufacturer's instructions.

Samples shall be analysed within 24 h after derivatization, as the stability of derivatives may fluctuate by humidity and side reactions. An aliquot of the solution is analysed by GC-MS.

Examples for a GC temperature program and a list of ions of the compounds are given in Annex B.

8.3.3 Calibration

Prepare solutions of different concentrations of levoglucosan, mannosan and galactosan by dissolving the substances in methanol or a mixture of methanol and dichloromethane. Add constant amounts of internal standard solution. Evaporate the solvent and carry out the derivatization with e.g. BSTFA/pyridine as described in 8.3.1.

The quotient of the peak areas of the analytes and the internal standard shall show a linear relation with the amount of analyte added.

9   Calculation of results

The peak areas of the substances (for IC-PAD), or the quotient of the peak areas of the internal standard and the substances (for GC-MS) of the samples are converted by the analytical software using the pertinent calibration function into concentrations of the solutions expressed as ng/g or ng/ml. The concentration (e.g. in ng/m^3) of the measured component in ambient air is calculated from these values and the sampling volume (Formula (1)).

$$C_x = \frac{c_x \cdot v_x}{V_s \cdot R_x}$$

(1)

where

$\quad C_x$ is the concentration of substance x in ambient air in ng/m^3;

$\quad c_x$ is the concentration of substance x in the solution after work up in ng/l;

$\quad v_x$ is the volume of the work up solution in l;

$\quad V_s$ is the volume of sampled air in m^3;

$\quad R_x$ is the work up or extraction efficiency of substance x.

NOTE R_x usually is approximately one. If quantification is performed using a surrogate standard, R_x corresponds to the recovery of the surrogate standard.

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