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FREE FORMALDEHYDE III (HPLC) ⧗ 212.0-96

RECOMMENDED TEST METHOD III: DETERMINATION OF FREE FORMALDEHYDE IN NONWOVENS BY LIQUID CHROMATOGRAPHY.

FOREWORD

The methods I, II and III (respectively ERT 210, 211 and 212) describe test methods for the evaluation of the formaldehyde content in nonwovens and precursor fibres under various conditions.
The method IV (ERT 213) describes a method for the release of formaldehyde during the processing of nonwovens.

- *Method I determines the amount of free formaldehyde and formaldehyde extracted partly through hydrolysis by means of a water extraction method.*

  This method is suitable for determination of contents above 20 mg/kg. It is based on the CEN / ISO standard: Textiles - Determination of formaldehyde - Part 1: Free and hydrolysed formaldehyde.

  The test conditions (40ºC) simulate the normal wearing conditions (consumer stage).

- *Method II determines the aggregate amount of free formaldehyde and the formaldehyde extracted partly through hydrolysis at stressed extraction conditions.*

  The testing conditions (80 ºC) simulate conditions encountered in some industrial applications.

  This method can also be used to accelerate the release of formaldehyde through hydrolysis by increasing the temperature. This simulates the behaviour of the sample over an extended period of time.

- *Method III determines the free formaldehyde using HPLC to overcome the interferences from coloured or formaldehyde-related species which can limit the usability of Methods I and II.*

  The conditions for extraction are specified in methods I and II.

- *Method IV determines the formaldehyde released by aqueous systems under defined drying conditions.*

  The aqueous systems tested are formaldehyde-containing or formaldehyde-cleaving systems that could be used in the bonding or finishing process of nonwovens.

- *Note: The AATCC 112 method [(1)] has been adopted as EN ISO 14184-2 standard: Textiles - Determination of formaldehyde - Part 2: Released formaldehyde (vapour absorption method).*
  This absorption method measures the propensity of a resin treated sample to liberate formaldehyde under prolonged hot humid conditions simulating garment processing or storage (garment makers stage).

(1) AATCC Technical Manual. American Association of Textile Chemists and Colourists. Method 112 - 1990.

1 SCOPE

This test method specifies a method for the determination of free formaldehyde extracted partly through hydrolysis. The method can be applied to the testing of nonwovens and precursor fibres.

The determination uses HPLC to overcome the interferences from coloured or formaldehyde-related species which can limit the usability of methods I and II.

The conditions for extraction are specified in methods I and II.

2 NORMATIVE REFERENCES

ERT 210 recommended test method I: Free and hydrolysed formaldehyde in nonwovens.

ERT 211 recommended test method II: Free and hydrolysed formaldehyde extracted at stressed extraction conditions.

ASTM D1193: Specification for Reagent Water.

ASTM E682: Practice for Liquid Chromatography Terms and Relationships.

ASTM D2194: Standard Test Method for Concentration of Formaldehyde Solutions.

3 PRINCIPLE

An aqueous extract from a nonwoven or precursor fibres in a water bath at 40°C (or 80°C) is chromatographed on a reversed-phase ODS column using an aqueous mobile phase and a photometric detector at 412 nm. Formaldehyde is separated from the other species in the matrix on a chromatographic column. The detection system includes a post-column reactor which produces a lutidine derivative when formaldehyde reacts with the 2,4-pentanedione reagent (Nash reagent). The concentration of free formaldehyde in the aqueous extracts is determined using peak areas from the standard and sample chromatograms (calibration by external standard). This method is specific for formaldehyde.

4 EQUIVALENT METHOD

The recommended method is based on the ASTM D5910: Standard Test Method for Determination of Free Formaldehyde in Emulsion Polymers by Liquid Chromatography.

5 WARNING

This method calls for the use of substances and / or procedures that may be injurious to health if adequate precautions are not taken. It refers only to technical suitability and does not absolve the user from legal obligations relating to health and safety at any stage. It has been assumed in the drafting of this method that the executing of its provisions is entrusted to appropriately qualified and experienced people.

6 COMMENTS ON THE METHOD

6.1 Significance and use

With the need to calculate free formaldehyde levels in above aqueous extracts, it is necessary to make the determination without upsetting any equilibria that might generate or deplete formaldehyde. This method provides a means for determining ppm levels of free formaldehyde in these extracts without upsetting any equilibria. The established working range of this method is 0,5 mg/kg to 15 mg/kg formaldehyde in the aqueous extract. Aqueous extracts can be diluted to meet the working range.

6.2 Interferences

This method is very selective for formaldehyde and potential interferences are either chromatographically separated from formaldehyde or do not react with the post-column reagent. The following species were identified as possible interferences for the method: acetaldehyde, acetone, benzaldehyde, formamide, formic acid, glyoxylic acid and propionaldehyde. These species, when chromatographed using this method, did not interfere with the formaldehyde peak at the 1000 ppm level.

6.3

Because nonwovens and precursor fibres vary in composition, the method run time may need to be extended to allow for late eluting compounds. Compounds which remain on the column after an analysis may interfere with the formaldehyde peak in subsequent runs.

7 APPARATUS

7.1 Liquid chromatograph

Any liquid chromatographic instrument having an injection valve, a post-column reactor, a 412 nm UV-VIS-detector, and an isocratic solvent delivery system may be used. The solvent delivery system must deliver a mobile phase flow of at least 0,6 ml/min.

(The UV-VIS-detector may incorporate either a tungsten lamp or a deuterium lamp with a second order visible filter that filters out light below 400 nm.)

7.2 Post-column reactor

Any post-column reactor that can deliver a reagent flow at 0,5 ml/min, contains a knitted reaction coil that can be heated to 95°C and contains a static mixing tee.

7.3 Chromatographic column

The column should be 250 x 4,6 mm internal diameter packed with reversed-phase pH stable C-18, 5 micron particles.

7.4 Chromatographic guard column

The column should be 10 x 4,6 mm internal diameter packed with reversed-phase pH stable C-18, 5 micron particles.

8 CONFIGURATION OF LIQUID CHROMATOGRAPH

An in-line check valve is place between the pump and the injector. The guard and analytical columns are connected to the injector. The outlet of the analytical column is connected to the mixing tee as described in section 9.

9 CONFIGURATION OF POST-COLUMN REACTOR (PCR)

The post-column reagent passes through a pulse-dampener and an in-line check valve prior to the mixing tee. The outlet of the analytical column is connected to one side of mixing tee. The reaction coil is connected to the outlet of the mixing tee. Stainless steel tubing with 0,25 mm internal diameter is used to make the connections. Tubing lengths should be kept to a minimum. The mixing tee and reaction coil are placed inside a 95°C oven. A 40 cm length of 0,25 mm internal diameter stainless steel tubing is connected to the outlet of the reaction coil and is placed in a ambient temperature stirred water bath. (This configuration acts as a heat exchanger.) The exit of the stainless steel tubing is connected to the UV-VIS-detector. Figure 1 shows a schematic of the system.

10 REAGENTS AND MATERIALS

10.1 Purity of reagents

Reagent grade chemicals shall be used with this method. Unless otherwise indicated, it is intended that all reagents shall conform to the specification of the Committee on Analytical Reagents of the American Chemical Society, where such specifications are available. Other grades may be used, provided it is first ascertained that the reagent is of sufficiently high purity to permit its use without lessening the accuracy of the determination.

10.2 Water

Unless otherwise indicated, references to water shall be understood to mean reagent water minimally conforming to Type II of Specification D1193, or distilled deionized water. HPLC grade water from chromatography suppliers is also acceptable.

10.3 Acetic acid, glacial (CH_3CO_2H)

10.4 Ammonium acetate ($CH_3CO_2NH_4$)

10.5 Acetylacetone (2,4-pentanedione) 99% ($CH_3COCH_2COCH_3$)

10.6 Formaldehyde solution of known content (determined by titration, approx. 36-37 g/100g)

10.7 Preparation of post-column reagent (Nash reagent)

62,5 g ammonium acetate were transferred into a 1 l amber volumetric flask that contains a stir bar. 600 ml water were added and mixed on a stir plate until the ammonium acetate is completely dissolved. After addition of 7,5 ml glacial acetic acid and 5 ml acetylacetone (2,4-pentanedione) the contents of the flask are diluted to volume with water and mixed thoroughly (45 min of mixing is suggested) until the ketone is dissolved completely.

2,4-pentanedione is light sensitive and should be protected from light during use.

The post-column reagent should be prepared weekly.

The post-column reagent is transferred to the post-column reactor reservoir. The reservoir should be protected from light. The post-column reagent has to be degassed with a helium sparge.

Note: The Nash reagent in this method has a concentration that is different from the concentration specified in methods I and II.

11 OPERATING CONDITIONS FOR ANALYSIS

Adjust the liquid chromatograph in accordance with the manufacturers directions and the following parameters. Allow the instrument to equilibrate until a stable base line is obtained on the data system.

Column temperature:	ambient
Mobile phase:	water (or 6,3 mM Na_2HPO_3) (pH=7)
Flow rate:	0,6 ml/min
Injection volume:	20µl
PCR temperature:	95°C
PCR flow rate:	0,3 ml/min
Detector:	UV/VIS, 412 nm

Determine whether the system is working properly by injecting 50 µl of a 10 ppm formaldehyde standard solution. A typical chromatogram of a 10 ppm formaldehyde standard obtained under the conditions outlined is shown in Fig. 2.

The peak asymmetry (A_S at 10% peak height) value for formaldehyde should be within the range of 0,8 and 1,7. A typical retention time for formaldehyde is 6 minutes.

The run time for the analysis is 10 min. The run time may have to be extended to 20 - 30 minutes if late eluting compounds interfere with the formaldehyde peak.

12 CALIBRATION AND STANDARDIZATION

Approximately 100 - 200 mg formaldehyde solution are weighed to the nearest 0.1 mg into a 100 ml flask. This solution is diluted to volume with water. This stock solution of formaldehyde is used for preparing standard solutions ranging from 0,05 to 15 ppm of formaldehyde in water for calibration.

The range of concentrations of the calibrating solutions has to cover the expected concentration of the test samples.

Stock and standard solutions should be stored in a refrigerator when not in use. The stock and standard solutions should be prepared weekly.

(Reagent grade formaldehyde is nominally 37%. Assay of the formaldehyde solution should be performed using ASTM method D2194.)

Calculate the calibration factor (CF) according to the following equation:

$$CF = \frac{A_S}{C_S} \quad [\mu V \times sec \times ml/mg]$$

where: A_S = area of formaldehyde peak of standard solution [µV x sec]
C_S = concentration of formaldehyde standard solution [mg/ml].

13 CALCULATION

Calculate the concentration of formaldehyde in the sample by using the above formula (method of external standard):

$$M_T = \frac{A_T}{CF \times C_T} \times 10^6$$

where:

M_T = amount of formaldehyde in test sample [mg / kg]
A_T = area of formaldehyde in test sample [µV x sec]
C_T = concentration of test sample in the injected solution [mg/ml].

14 REPORT

The test report shall include the following information:

a) Test method used.

b) Description of the sample tested.

c) Conditions of extraction.

d) Amount of formaldehyde extracted.

e) Result from the blank test.

f) Any deviation from the standard procedure.

15 NOTES

Note 1: The apparatus and operating parameters may be varied to suit specific circumstances (e.g. an other column diameter - 4 or 5 mm - can be used but the flow rate specified in 11 has to be adapted accordingly). It must be ascertained that any such variations do not have an adverse effect on the results obtained (validation). Any deviation from the standard method must be recorded and mentioned in the report.

Note 2: In well validated conditions, pre-column derivatisation can be used. This should be mentioned in the report.

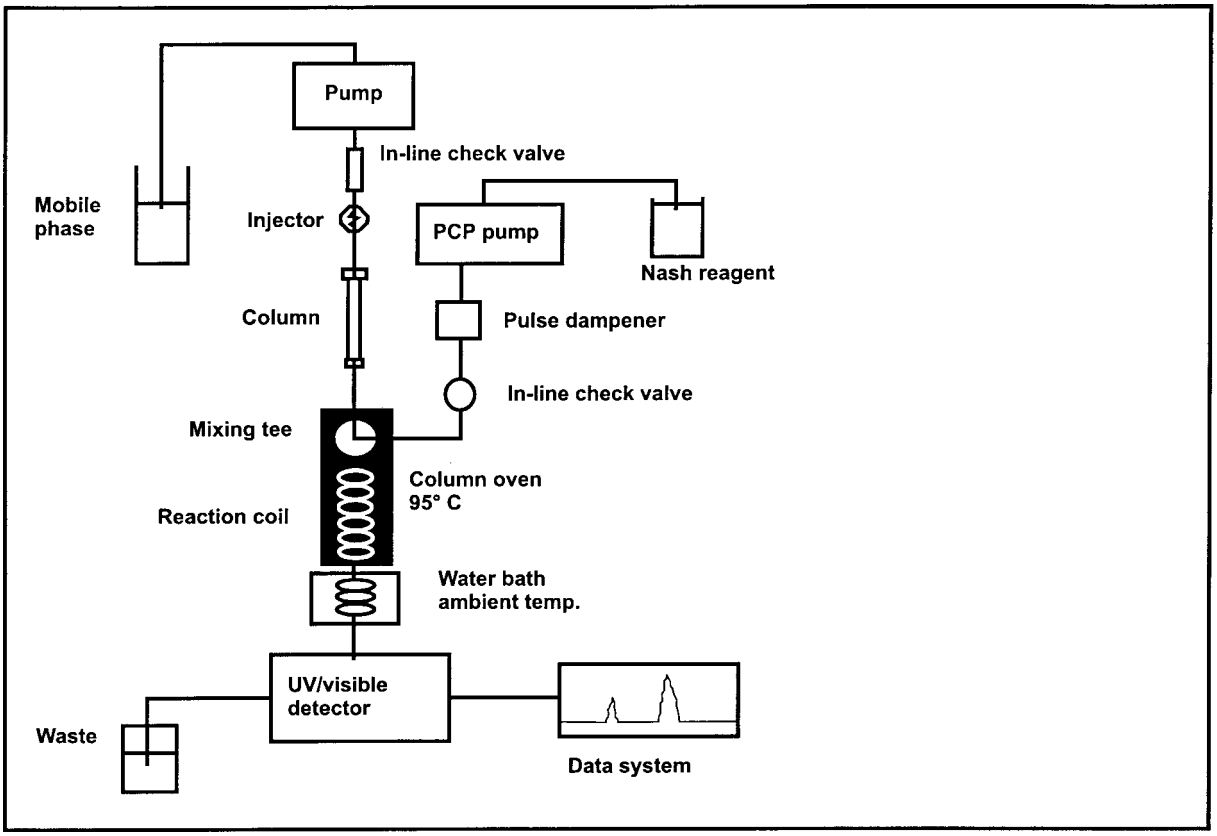

Figure 1 - Configuration of liquid chromatograph

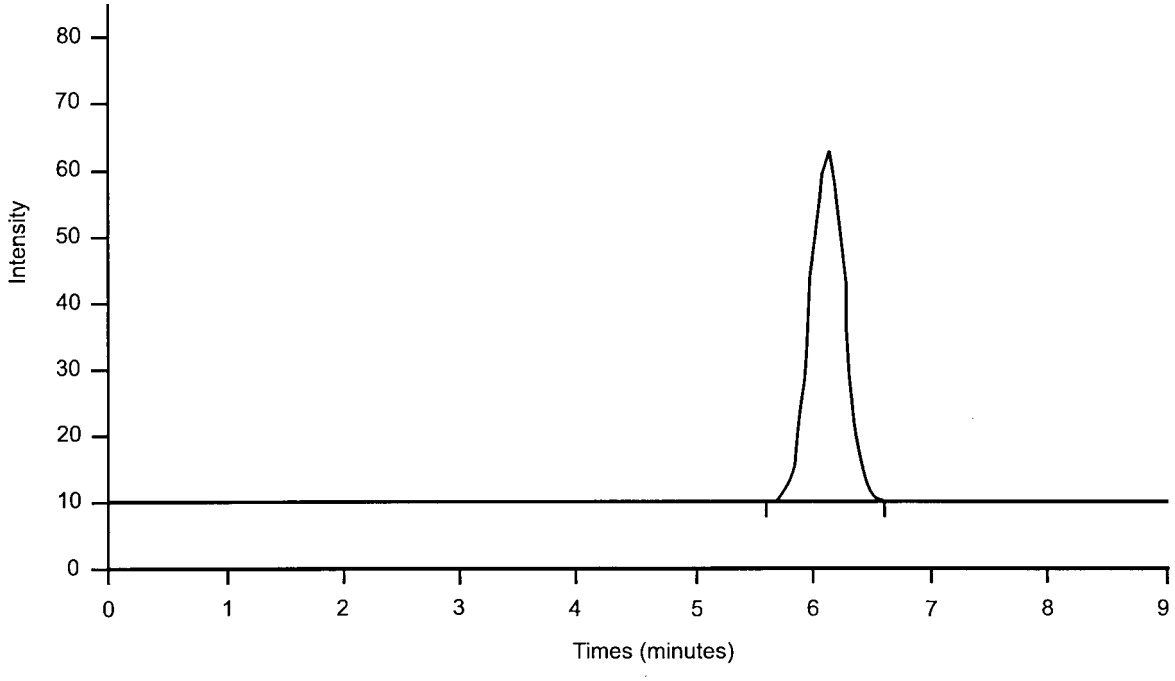

Figure 2 - Formaldehyde