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Protective gloves — The determination of Dimethylformamide in gloves

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National foreword

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

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Protective gloves - The determination of Dimethylformamide in gloves

Gants de protection - Détermination de la teneur en diméthylformamide dans les gants

Schutzhandschuhe - Bestimmung von Dimethylformamid in Handschuhen

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European foreword

This document (EN 16778:2016) has been prepared by Technical Committee CEN/TC 162 “Protective clothing including hand and arm protection and lifejackets”, the secretariat of which is held by DIN.

This European Standard shall be given the status of a national standard, either by publication of an identical text or by endorsement, at the latest by September 2016, and conflicting national standards shall be withdrawn at the latest by September 2016.

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1 Scope

This document specifies a test method for the determination of Dimethylformamide (DMFa – CAS N° 68-12-2) in glove materials.

NOTE For Dimethylformamide the following abbreviations can be used: DMF, ***DMFa*** DMFo.

The test method is applicable for the following materials:

— polyurethane (PU) materials (except elastane), PU Coated material (textile, leather), PU foam, PU blended materials;

— adhesives;

— all materials manufactured with a dipping process using DMFa.

2 Normative references

Not applicable.

3 Principle

The sample is cut into small pieces and extracted with methanol in a sealed flask in an ultrasonic bath. An aliquot of the extract is analysed with GC-MS.

4 Consumables

4.1 Reagents

The substances are given in Table 1.

Table 1 — Reagent used in analysis

N°	Substances	CAS-Nr.	purity
1	N, N-Dimethylformamide (DMFa)	68–12–2	Certified standard (purity 95 % at least)
2	Dimethylformamide-d7 (DMFa-d7)	4472–41–7	Certified standard (purity 95 % at least)
3	Methanol	67–56–1	analytical grade (purity 99 % at least)

4.2 Stock solutions

4.2.1 Internal standard — Stock solution (1000 mg/l)

100 mg of DMFa-d7 is weighed with an accuracy of 0,1 mg in a 100 ml volumetric flask and filled with methanol to the mark and stored at 4 °C, for maximum 1 month.

4.2.2 Internal standard — working solution (200 mg/l)

The solution is prepared by 1:5 dilution of the stock solution (4.2.1) with methanol. Storage conditions maximum of 1 month at 4 °C.

4.2.3 Target compound — Stock solution (1000 mg/l)

100 mg of DMFa is weighed with an accuracy of 0,1 mg in a 100 ml volumetric flask and filled up to the mark with methanol and stored at 4 °C for maximum 1 month.

4.2.4 Target compound — working solution (200 mg/l)

The solution is prepared by 1:5 dilution of the stock solution (4.2.3) with methanol. Storage conditions maximum of 1 month at 4 °C.

4.2.5 Extraction solution containing 20 mg/l internal standard

Add 100 ml internal standard — working solution (4.2.2) in a 1000 ml volumetric flask and fill it with Methanol to the 1000 ml calibration mark. This solution can be stored in a vessel at 4 °C for 6 months.

5 Equipment

Usual lab equipment, in addition:

5.1 **analytical balance** (precision at least 0,1 mg);

5.2 **sealed flask** (for instance, Erlenmeyer) with screw cap and polytetrafluoroethylene (PTFE) seal, 250 ml;

5.3 **ultrasonic bath** capable of maintaining a temperature of (70 ± 5) °C;

5.4 **PTFE-membrane filter** pore width 0,45 µm;

5.5 suitable **sample vials** with PTFE-capped for GC-MS analysis;

5.6 **volumetric flask**, 10 ml, 100 ml, 1000 ml;

5.7 range of **micropipettes** and dispenser with volume between 20 µl to 200 ml;

5.8 **gas chromatograph** with mass detector.

6 Test procedure

6.1 Sampling

The sample shall consist of a least a pair of gloves.

6.2 Conditioning

When the gloves are received, the laboratory shall package them into an airtight plastic sealed bag (e.g. polyethylene bag) before the start of the preparation steps. Vacuum sealer shall not be used.

If stored for more than 24 h before testing, the gloves shall be kept at (4 ± 3) °C.

NOTE During the validation interlaboratory test, it has been demonstrated that a15 day's storage in sealed plastic bag at 4 °C has shown no significant difference in results.

The sample (in the seal plastic bag) shall be conditioned (24 ± 1) hours at (23 ± 2) °C prior to the preparation.

6.3 Preparation

The sample is removed from the plastic bag.

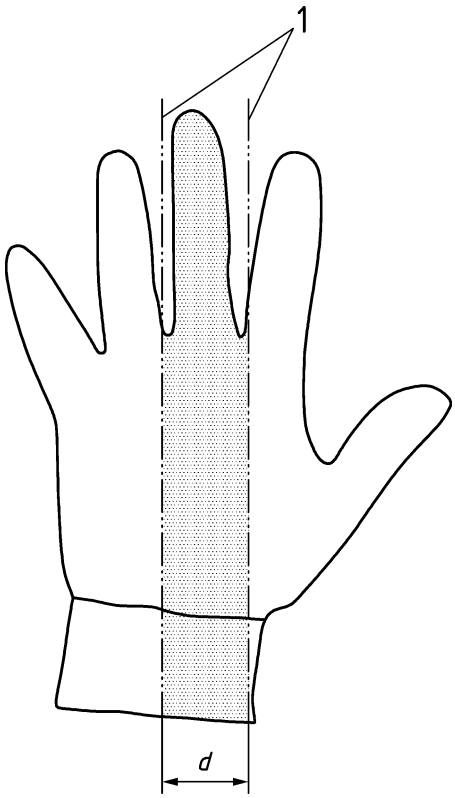
Cut a piece as shown in Figure 1 from each glove of the pair to have 2 test pieces.

Each test pieces is a full finger including the strips from the palm and the back of the glove.

The sampling is carried out so that all materials are included.

Cut each of the 2 test pieces into pieces of about 10 mm by 10 mm.

Immediately after use an analytical balance (5.1) to weigh each of the 2 cut up test pieces to an accuracy of 0,1 g.



Key:

1 cut

d (30 ± 5) mm

NOTE The shaded area is the test piece

Figure 1 — Cutting of the test piece

6.4 Extraction

The extraction shall be started maximum (30 ± 5) minutes after the weighing of the tests pieces.

Each test piece is put in a 250 ml Erlenmeyer flask. (5.2). Add the stored extraction solution (4.2.5) at a ratio of 10,0 ml per 1,0 g cut up test piece. The closure is to maintain safe and gas tight, throughout the complete extraction.

The sample is then extracted 30 min at a temperature of 70 °C in an Ultrasonic bath.

WARNING — Extraction at 70 °C leads to overpressure and the risk of uncontrolled emission of Methanol and loss of DMFa.

After cooling to room temperature, the solution is filtered through a PTFE membrane filter (5.4). An aliquot of the extract is transferred to a GC-MS vial and sealed with a PTFE-cap (5.5).

The sealing should be done by well-trained operator to avoid any leakage.

6.5 Determination with GC-MS

6.5.1 Calibration

Five calibrations points are used to establish the calibration curve, they are all prepared in 10 ml volumetric flasks, as stated in Table 2. A 6th point, L_0, a blank, shall be included in the calibration curve.

Table 2 — Preparation of calibration

Standard	L1	L2	L3	L4	L5
Volume of target compound working solution (4.2.4) in µl	25	50	100	250	500
Conc. of target compound in the solution in mg/l	0,5	1	2	5	10
Volume of the of internal standard working solution (4.2.2) in µl	1000	1000	1000	1000	1000
Concentration of the internal standard in mg/l	20	20	20	20	20
Standard	L_1	L_2	L_3	L_4	L_5
Volumetric flasks are filled to the mark with methanol					

6.5.2 Examples of instrumental method

6.5.2.1 Measuring method

Suggested parameters for GC-MS determination of DMFa.

Measuring parameter: The DMFa is analysed by gas chromatography/mass spectrometry on a single quad/MS use in a simultaneous SIM/SCAN mode.

6.5.2.2 Chromatographic conditions

a) COLUMN:

- polar stationary phase based on Polyethylene Glycol;
- length: 30 m;
- internal diameter: 250 µm;

— film thickness: 0,5 µm;

— (alternative column possible as long as it has the same properties).

b) CARRIER GAS:

— helium.

c) OVEN:

— 60 °C during 2 min;

— 250 °C at 20 °C/min;

— 250 °C during 2 min.

d) INJECTOR:

— 240 °C in splitless mode with an injection volume of 1 µl.

6.5.2.3 Detection conditions

a) TRANSFER LINE: 240 °C:

— The single quad MS work in simultaneous SIM/SCAN mode;

— The mass SCAN range is between 40 to 200 uma.

Table 3 — The SIM mode focus on the following ions

Compounds	Ions
DMFa	73 (quantifier)
	44 (qualifier)
DMFa-d7	80 (quantifier)

6.6 Quantification

The DMFa content is calculated according to the following equation as a mass fraction w in mg/kg of glove.

Set up the linear regression function by using the following ratio (A_e/A_{is}) and (C_e/C_{is}) with the help of the formula:

$$\left(\frac{A_{\mathrm{e}}}{A_{\mathrm{is}}}\right) = a \times \left(\frac{C_{\mathrm{e}}}{C_{\mathrm{is}}}\right) + b$$

Where:

— A_e is the area of the peak of Dimethylformamide;

— A_{is} is the area of the peak of Dimethylformamide-D7;

— C_e is concentration of Dimethylformamide in the calibration standard in microgram per litter;

— C_{IS} is concentration of Dimethylformamide-D7 in the calibration standard in microgram per litter;

— a is the slope of the linear function;

— b is the ordinate intercept of the calibration curve, in mg/l.

The content of DMFa is calculated according to the following equation as a mass fraction w in mg/l:

$$W = \left(\frac{V}{m}\right) \times \frac{\frac{A_{\text{ech}}}{A_{\text{is}}} - b}{a} \times C_{\text{is}}$$

Where:

— W is the content of the Dimethylformamide in the specimen (mg/l);

— V is the volume of the solvent use for the extraction (ml) (in most cases, this value will be equal to 10 ml);

— m is the mass of the tested specimen (g);

— A_{ech} is the area of the peak of Dimethylformamide in the sample;

— A_{is} is the area of the peak of Dimethylformamide-D7 in the sample;

— C_{IS} is concentration of Dimethylformamide-D7 in the sample in microgram per litter;

— a is the slope of the linear function;

— b is the ordinate intercept of the calibration curve. The units depend of the evaluation.

6.7 Results

Each determination result shall be reported.

The final result is the average (Mv) of the 2 values obtained on the 2 test pieces.

7 Performance of the method

Quantification limit of this test method is 5 mg/kg of DMFa in gloves or glove components.

8 Test report

The test report shall include at least the following:

— reference to this standard;

— description of the packaging at reception;

— all details necessary for complete identification of the sample tested;

— date of reception of the sample in the laboratory;

— date of the test;

— condition and time of storage before the test in the laboratory;

— used analytical technic;

— the determined content of the extracted DMFa is given in ppm (see 6.7);

— any deviation from the present standard.

Annex A
(informative)

Results of the interlaboratory trial

The following data have been obtained in a collaborative correlation trial organized by CEN/TC 162 WG 8 in November/December 2013 with a group of relevant laboratories (on demand from CEN/TC 162 secretariat).

Table A.1 — Results of correlation trial

	Number of laboratories	Number of measurement per laboratory	Average value	Standard deviation
Spiked sample with 10ppm	8	1	12,5	7,0
Spiked sample with 200ppm	5	1	197,7	8,0
Dipped Polyurethane test pieces with dynema	5	4	33,7	5,3
Dipped Polyurethane test pieces with nylon	7	4	761,4	130,9

Bibliography

CEN ISO/TS 16189, *Footwear - Critical substances potentially present in footwear and footwear components - Test method to quantitatively determine dimethylformamide in footwear materials (ISO/TS 16189:2013)*

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