भारतीय मानक
Indian Standard

IS 16552 : 2017

वस्त्रादि सहायक — हाई परफॉरमेंस द्रवक्रोमैटोग्राफी पद्धति द्वारा फॉर्मल्डीहाइड की मात्रा ज्ञात करने की रासायनिक विधि

Textile Auxiliaries — Chemical Determination of Formaldehyde Content — Method Using High Performance Liquid Chromatography

ICS 59.080.01

भारतीय मानक ब्यूरो
BUREAU OF INDIAN STANDARDS
मानक भवन, 9 बहादुरशाह ज़फर मार्ग, नई दिल्ली-110002
MANAK BHAVAN, 9 BAHADUR SHAH ZAFAR MARG
NEW DELHI-110002
www.bis.org.in www.standardsbis.in

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FOREWORD

This Indian Standard was adopted by the Bureau of Indian Standards, after the draft finalized by the Chemical Methods of Test Sectional Committee and approval of the Textile Division Council.

Various textile auxiliaries like polyvinyl alcohol, binder, resins, dye fixing agents, softeners etc, are used in textile industry to impart certain aesthetic values to textile items. Many Indian Standards on textile auxiliaries like IS 13948, IS 13949, IS 13950 and IS 14699 etc, have been formulated which also specifies the requirements of 'Free Formaldehyde Content' and 'Total Formaldehyde Content' to be determined by the titrametric methods. At present, titrimetric methods for analyzing 'Free Formaldehyde Content' and 'Total Formaldehyde Content' in textile substrate are not suitable for textile auxiliaries due to interference of matrics. Therefore, an extraction method has been standardized to extract formaldehyde from various textile auxiliaries and then measuring the Formaldehyde Content by HPLC. By this method, formaldehyde content in textile auxiliaries can be determined up to 1.0 ppm level.

High concentration of the formaldehyde in textile auxiliaries causes health hazards in human beings, resins finished fabric become susceptible to chlorine damage after hypo chloride bleaching and due to very pungent order, stitching of the garments becomes difficult.

In preparing this standard, considerable assistance has been derived from :

ISO 17226-1 : 2008(E) 'Leather — Chemical determination of formaldehyde content — Part 1 : Method using High performance liquid chromatography'

ISO 14184-1: 2011(E) 'Textiles — Determination of formaldehyde — Part 1: Free and hydrolized formaldelyde (Water extraction method)'

For the purpose of deciding whether a particular requirement of this standard is compiled with, the final value, observed or calculated, expressing the result of a test or analysis, shall be rounded off in accordance with IS 2 : 1960 'Rules for rounding off numerical values (*revised*)'. The number of significant places retained in the rounded off value should be the same as that of the specified value in this standard.

Indian Standard

TEXTILE AUXILIARIES — CHEMICAL DETERMINATION OF FORMALDEHYDE CONTENT — METHOD USING HIGH PERFORMANCE LIQUID CHROMATOGRAPHY

1 SCOPE

This standard specifies a test method for the determination of free and released formaldehyde in textile auxiliaries. This method is based on High Performance Liquid Chromatography (HPLC). It is a selective and not sensitive to coloured extracts. The formaldehyde content is taken to be the quantity of free formaldehyde and formaldehyde extracted through hydrolysis contained in a water extract from the auxiliaries under standard conditions. Formaldehyde content in auxiliaries like polyvinyl alcohol, Binder, Resin, Dye fixing agent, Softener etc, have been standardized by this method.

2 REFERENCES

The following Indian Standards are necessary adjuncts to this standard.

IS No.	*Title*
3321 : 1973	Specification for formaldehyde solution (*first revision*)
1070 : 1992	Reagent grade water — Specification (*third revision*)

3 TERMINOLOGY

3.1 For the purpose of this standard the following terms and definitions shall apply.

3.1.1 *Retention Time* — Retention time is the time it takes in minutes after sample injection for the analyte peak to reach the detector.

3.1.2 *Peak Area* — Peak area is the area (mAu*s) under the peak curve.

3.1.3 *Peak Spectrum* — A peak spectrum is the absorption band throughout the ultra-violet region of the analyte.

4 PRINCIPLE

4.1 Formaldehyde is extracted under specified condition and is separated and quantified as a derivative of 2,4-DNPH (Di Nitro Phenyl Hydrazine) by High Performance Liquid Chromatography (HPLC) using a photo diode array detector. Aldehydes and ketones react with 2,4-DNPH (Dinitrophenyl hydrazine)and converts their respective hydrazones which will give an absorption peak at 360 nm wave length.

5 REAGENTS

5.1 Formaldehyde Solution, approximately 37.0 percent (mass *m/m*)

5.2 Sodium Sulphite, 1.0 mol/litre

5.3 Thymolphthalein Indicator

5.4 Sulfuric Acid, 0.01 mol/litre

5.5 Distilled Water, Grade 3

5.6 2, 4 Dinitrophenyl Hydrazine Solution, consisting of 0.3 g DNPH dissolved in 100 ml concentrated *O*-phosphoric acid (85 percent mass fraction).

5.7 Acetonitrile (HPLC grade).

6 APPARATUS

6.1 Volumetric Flasks, 10 ml, 100 ml, 500 ml and 1 000 ml capacities.

6.2 Erlenmeyers Flasks, 100 ml and 250 ml capacities.

6.3 Syringe Filter (0.2 µm disposable nylon membrane filter).

6.4 Glass Beakers, 100 ml capacity.

6.5 Graduated Pipette, 10 ml capacities.

6.6 Analytical Balance, weighing to an accuracy of 0.1 mg.

6.7 Ultrasonic Water Bath, capable to maintain 30 ± 5°C.

6.8 HPLC system with photo diode array detector at 360 nm wave length.

7 PROCEDURES FOR CALIBRATION

7.1 Preparation and Standardization of Formaldehyde Stock Solution

Prepare an approximately 1 500 mg/l stock solution of formaldehyde by diluting 3.8 ml of formaldehyde solution to one litre with distilled water. Determine the concentration of formaldehyde in the stock solution by standard method as per IS 3321. Record the accurate

concentration of formaldehyde in this standard stock solution. This stock solution will keep for up to four weeks when stored at 4°C and appropriately stopped and is used to prepare standard dilutions.

7.2 Calibration of HPLC

Pipette 1.0 ml of the formaldehyde stock solution obtained in (**7.1**) with an exactly known formaldehyde content into a 100 ml volumetric flask and fill to the mark with water. This solution (approximately 15.0 µg/ml) is the standard solution for calibration purpose.

In each of six 10 ml volumetric flask, add 4 ml of acetonitrile, then add a series of 0.5 ml, 1.0 ml, 2.0 ml, 3.0 ml, 4.0 ml, and 5.0 ml respectively of the standard formaldehyde solution. Immediately upon addition of formaldehyde solutions add 0.5 ml DNPH solution. Fill the flask up to the mark with distilled water and mix. Keep the flasks at room temperature for 1 h and analyze the standards using HPLC as per the conditions given in **7.4.3**. Effect the calibration through plotting a graph of the formaldehyde derivative peak areas *versus* the concentration in ìg/ml. The concentration of formaldehyde thus plotted will be in the range of 0.75 µg/ml-7.5µg/ml. If the regression coefficient (r^2) of the calibration graph is found to be less than 0.99, repeat the calibration with fresh standards. Construct one blank in a similar way but without formaldehyde. Inject blank and ensure that no formaldehyde peak detected in the blank sample. In blank there will be only one peak of DNPH of about 3.5 min retention time. Standard chromatogram will contain two peaks, the first peak will be DNPH followed by formaldehyde derivative of about 5.5 min retention time (Annex A Fig. 1).

7.3 System Suitability

Inject one standard repeatedly 5 times and calculate the response factor (*Rf*) in each time. Calculate the standard deviation of *Rf*. The standard deviation of *Rf* should not be more than 2.0 percent.

Response factor (*Rf*) = Area of the peak / Concentration

7.4 Procedure for the Determination of Formaldehyde in Auxiliaries by the HPLC Method

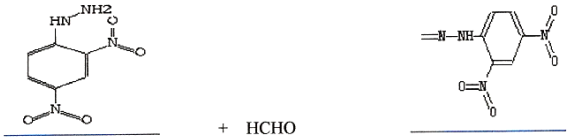
7.4.1 *Extraction*

Weigh 2.0 ± 0.1 g auxiliary in a glass beaker and dissolve in distilled water and transfer into 100 ml of volumetric flask. Fill the flask up to the mark with distilled water and keep in an ultrasonic bath at 30°C ± 5 for 10 min ± 1.

7.4.2 *Derivatization of Formaldehyde with DNPH* (*2.4 Dinitrophenyl Hydrazine Solution*)

Pipette 4.0 ml of acetonitrile, a 5.0 ml aliquot of the sample extract (**7.4.1**) and 0.5 ml of DNPH solution (0.3 percent in ortho phosphoric acid) into a 10 ml volumetric flask. Fill the volumetric flask with distilled water up to the mark and shake briefly by hand to mix the components. Allow it to stand at least 60 min. After filtering through a 0.2 µm membrane nylon filter, analyze the sample using HPLC as per the condition (**7.4.3**). Record the retention time and the peak areas of the formaldehyde, dinitrophenyl hydrazone peak. Calculate the formaldehyde concentration from the standard calibration graph. Compare the peak spectra of the standard formaldehyde and sample for confirmation (Annex A Fig. 2). If the concentration is out of the calibration range, take smaller aliquots or appropriate dilutions. Recovery rate of formaldehyde shall be determined as per method given at Annex B.

Reaction between formaldehyde and 2,4 DNPH is given as below



2,4 DNPH [HYDRAZINE] — 2,4 DNPH [HYDRAZONE]

7.4.3 *HPLC Conditions*

Mobile phase	Acetonitrile/Water, 60/40
Flow rate	1.0 ml/min
Separation column	C 18 reversed phase column (250 mm× 4.6 mm × 5.0 µm)
Diode array detector wave length	360 nm
Slit width/Band width	8 nm/8 nm
Column temperature	40°C
Injection volume	20 µl

7.4.4 *Calculation of Formaldehyde Content in Auxiliary Samples*

$$wF = \frac{Ps \times F}{m}$$

where

wF = concentration of formaldehyde in auxiliary sample in µg/kg;

Ps = concentration of formaldehyde (µg/ml) obtained from the calibration graph;

F = dilution factor in ml;

m = weight in gram of sample.

8 EXPRESSION OF RESULTS

Express the formaldehyde concentration to the nearest 0.1 mg/kg based on the mass of the sample tested.

ANNEX A

(*Clauses* 7.2 *and* 7.4.2)

IDENTIFICATION OF FORMALDEHYDE FROM OTHER ALDEHYDES AND KETONES

All aldehydes and ketones reacts with 2,4 DNPH and derivatize their corresponding hydrazones. The hydrazone of aldehyde and ketones exhibit a unique spectrum in the ultraviolet region (190-380 nm) and can be distinguish without any ambiguity. For confirmation purpose one should compare the ultraviolet spectra of standard formaldehyde and sample if the retention time is found to be the same (Fig. 2). This is to avoid reporting false positive results.

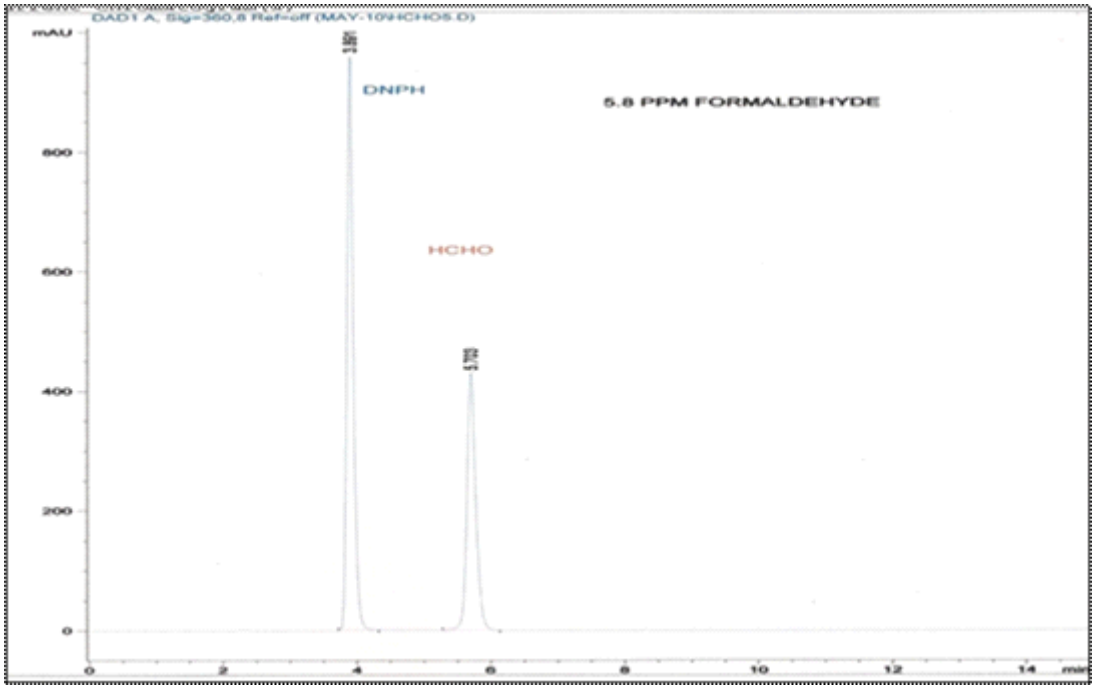


FIG 1 CHROMATOGRAM OF FORMALDEHYDE (DNPH)

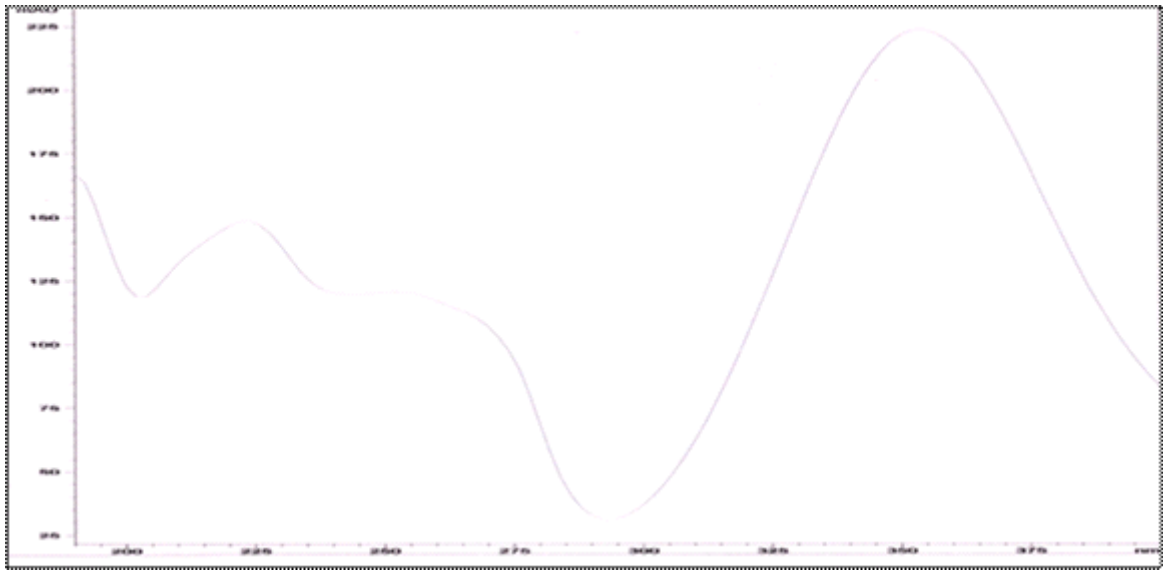


FIG 2 UV SPECTRA OF FORMALDEHYDE (DNPH)

ANNEX B

(*Clause* 7.4.2)

SPIKING-DETERMINATION OF RECOVERY RATE

B-1 Three known level of formaldehyde in the range of 10-100 ppm, 100-250 ppm and 500 -1 000 ppm was spiked in water, polyvinyl alcohol, Binder, Softener, Dye fixing agent and Resin. The spiked auxiliaries were extracted with ultrasonic water bath at 30 ± 5°C for 10 min. An aliquot of the extract was treated with DNPH and analyzed by HPLC as per the method given in **7.4.3** and recovery rate was calculated.

Table 1 indicates the percentage recovery of formaldehyde from various auxiliaries.

B-2 Inter Laboratory Comparison

The following data has been obtained (Table 2 and Table 3) in a collaborative trial with five laboratories on different textile auxiliaries sample with unknown level of formaldehyde.

Table 1 Recovery Data of Formaldehyde from Auxiliaries

Sl No.	Spiked Auxiliaries	Recovery (%) in Ultrasonic Water Bath Extraction
i)	Water	99.0-99.7
ii)	Polyvinyl alcohol	97.6-99.3
iii)	Binder	93.0-97.1
iv)	Resin	92.7-95.3
v)	Dye fixing agent	93.2-96.2
vi)	Softener	91.1-98.1

Table 2 Inter Laboratory Comparison of Results

Auxiliaries Sample Code	Laboratory Code Formaldehyde (ppm)									
	Lab-A	Lab-B	Lab-C	Lab-D	Lab-E	Median	Lower quartile	Upper quartile	IQR	IQR × 0.741 3
1-A	21 275	14 598	22 971	26 197	15 666	21 275	15 666	22 971	7 305	5 415.2
1-D	3 241	2 302	3 152	4 939	2 053	3 152	2 302	3 241	288	213.5
C-2	306	117	306	283	181	283	181	305	124	91.9
D-4	54.7	17	37	201	26	37	26	54	28	20.8

Table 3 Z Score Values of Inter Laboratory Comparison

Auxiliaries Sample Code	Participated Laboratories and Lab Code				
	Lab-A	Lab-B	Lab-C	Lab-D	Lab-E
1-A	0.00	-1.23	0.31	0.91	-1.04
1-D	0.12	-1.2	0.0	2.5	-1.58
C-2	0.24	-1.81	0.25	0.00	-1.11
D-4	0.82	-0.96	0.0	7.90	-0.53

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Amendments Issued Since Publication

Amend No.	Date of Issue	Text Affected

BUREAU OF INDIAN STANDARDS

Headquarters:

Manak Bhavan, 9 Bahadur Shah Zafar Marg, New Delhi 110002
Telephones : 2323 0131, 2323 3375, 2323 9402 *Website*: www.bis.org.in

Regional Offices: *Telephones*

Central : Manak Bhavan, 9 Bahadur Shah Zafar Marg, NEW DELHI 110002 — 2323 7617, 2323 3841

Eastern : 1/14 C.I.T. Scheme VII M, V. I. P. Road, Kankurgachi, KOLKATA 700054 — 2337 8499, 2337 8561, 2337 8626, 2337 9120

Northern : Plot No. 4-A, Sector 27-B, Madhya Marg, CHANDIGARH 160019 — 26 50206, 265 0290

Southern : C.I.T. Campus, IV Cross Road, CHENNAI 600113 — 2254 1216, 2254 1442, 2254 2519, 2254 2315

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