भारतीय मानक

Indian Standard

IS 14575 : 2024
ISO 17070 : 2015

चमड़ा — रासायनिक परीक्षण — टेट्राक्लोरोफेनोल-, ट्राइक्लोरोफेनोल-, डाइक्लोरोफेनोल-, मोनोक्लोरोफेनोल- आइसोमर्स और पेंटाक्लोरोफेनोल मात्रा का निर्धारण

(पहला पुनरीक्षण)

Leather — Chemical Tests — Determination of Tetrachlorophenol - ,Trichlorophenol-, Dichlorophenol-, Monochlorophenol- Isomers and Pentachlorophenol Content

(*First Revision*)

ICS 59.140.35

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

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Leather, Tanning Material and Allied Products Sectional Committee, CHD 17

NATIONAL FOREWORD

This Indian Standard (First Revision) which is identical to ISO 17070 : 2015 'Leather — Chemical tests — Determination of tetrachlorophenol-, trichlorophenol-, dichlorophenol-, monochlorophenol-isomers and pentachlorophenol content' issued by the International Organization for Standardization (ISO), was adopted by the Bureau of Indian Standards on the recommendation of the Leather, Tanning Materials and Allied Products Sectional Committee and approval of the Chemical Division Council.

This standard was first published in 1999. The Committee responsible for formulating this standard has decided to revise the standard and harmonize the standard with latest ISO standard ISO 17070 : 2015. This standard specifies a method for determining the content of tetrachlorophenol-, trichlorophenol-, dichlorophenol-, monochlorophenol-isomers, and pentachlorophenol, its salts, and esters in leather.

The text of ISO standard has been approved as suitable for publication as an Indian Standard without deviations. Certain conventions and terminologies are, however, not identical to those used in Indian Standards. Attention is particularly drawn to the following:

a) Wherever the words `International Standard' appear referring to this standard, they should be read as `Indian Standard'; and

b) Comma (,) has been used as a decimal marker in the International Standard, while in Indian Standards, the current practice is to use a point (.) as the decimal marker.

In this adopted standard, reference appears to certain International Standards for which Indian Standards also exist. The corresponding Indian Standards, which are to be substituted in their respective places, are listed below along with their degree of equivalence for the editions indicated:

International Standard	*Corresponding Indian Standard*	*Degree of Equivalence*
ISO 4044 Leather — Chemical tests — Preparation of chemical test samples	IS 16256 : 2022/ ISO 4044 : 2017 Leather — Chemical tests — Preparation of chemical test samples	Identical
ISO 4684 Leather — Chemical Tests — Determination of Volatile Matter	IS 582 (Part 1) : 2017/ISO 4684 : 2005 Method of chemical testing of leather: Part 1 Determination of volatile matter (*second revision*)	Identical

In this adopted standard, the reference appears to certain International Standards for which Indian Standards exists. So, the technical committee has reviewed the provisions of the following International Standards documents referred in this adopted standard and has decided that they are acceptable for use in conjunction with this standard:

International Standard	*Title*
ISO 2418	Leather — Chemical, physical, mechanical and fastness tests — Position and preparation of specimens for testing
ISO 3696	Water for analytical laboratory use — Specificationand test methods

(*Continued on third cover*)

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Introduction

This International Standard describes a procedure where the chlorinated phenols (CP) are acetylated before the chromatographic detection and the amount of the detected chlorinated phenyl acetate is quantified via an internal standard correction.

Indian Standard

LEATHER — CHEMICAL TESTS — DETERMINATION OF TETRACHLOROPHENOL-,TRICHLOROPHENOL-, DICHLOROPHENOL-, MONOCHLOROPHENOL- ISOMERS AND PENTACHLOROPHENOL CONTENT

(*First Revision*)

1 Scope

This International Standard specifies a method for determining the content of tetrachlorophenol-, trichlorophenol-, dichlorophenol-, monochlorophenol-isomers, and pentachlorophenol, its salts, and esters in leather.

NOTE Bromophenol isomers can also be determined using this method.

2 Normative references

The following documents, in whole or in part, are normatively referenced in this document and are indispensable for its application. For dated references, only the edition cited applies. For undated references, the latest edition of the referenced document (including any amendments) applies.

ISO 2418, *Leather — Chemical, physical and mechanical and fastness tests — Sampling location*

ISO 3696, *Water for analytical laboratory use — Specification and test methods*

ISO 4044, *Leather — Chemical tests — Preparation of chemical test samples*

ISO 4684, *Leather — Chemical tests — Determination of volatile matter*

3 Abbreviations

The following abbreviations are used for chlorinated phenols in this International Standard:

CP chlorinated phenols

DiCP dichlorophenol

MoCP monochlorophenol

PCP pentachlorophenol

TCG tetrachloroguaiacol (tetrachloro-*o*-methoxyphenol)

TeCP tetrachlorophenol

TriCP trichlorophenol

4 Principle

First of all, the leather sample is submitted to steam-distillation.

After extraction into *n*-hexane, the chlorinated phenols (CP) are acetylated by acetic anhydride and the chlorinated phenyl acetates are analysed by gas-chromatography with an electron capture detector (ECD) or mass selective detector (MSD). Quantification is performed by an external standard and a correction made with an internal standard.

5 Apparatus

5.1 Gas chromatography (GC), with ECD or MSD detector.

5.2 Analytical balance, weighing to an accuracy of 0,1 mg.

5.3 Suitable apparatus designed for steam distillation.

5.4 Shaking machine, capable of at least 200 cycles per minute.

5.5 Volumetric flasks, 500 ml and 50 ml.

5.6 Erlenmeyer (conical) flask, 100 ml.

5.7 Separating funnel, 250 ml, or **suitable vessel that allows separation of organic and aqueous phases**, that can be sealed for vigorous shaking.

5.8 Pasteur-pipettes, graduated pipettes, suitable auto-pipettes.

5.9 Strainer with paper filter, grade 4, diameter 125 mm.

6 Reagents

Unless otherwise specified, analytical grade chemicals should be used. Water shall be distilled or deionized, Grade 3 in accordance with ISO 3696.

6.1 Chlorinated phenol mix

A mix of the chlorinated phenols which contains the following isomers at a concentration of 100 µg/ml in acetone.

2-Chlorophenol	CAS[1)]-Number: 95–57–8
3-Chlorophenol	CAS-Number: 108–43–0
4-Chlorophenol	CAS-Number: 106–48–9
2,3-Dichlorophenol	CAS-Number: 576–24–9
2,4-Dichlorophenol	CAS-Number: 120–83–2
2,5-Dichlorophenol	CAS-Number: 583–78–8
2,6-Dichlorophenol	CAS-Number: 87–65–0
3,4-Dichlorophenol	CAS-Number: 95–77–2
3,5-Dichlorophenol	CAS-Number: 591–35–5
2,3,4-Trichlorophenol	CAS-Number: 15950–66–0
2,3,5-Trichlorophenol	CAS-Number: 933–78–8
2,3,6-Trichlorophenol	CAS-Number: 933–75–5

1) CAS Chemical Abstracts Service.

2,4,5-Trichlorophenol	CAS-Number: 95–95–4
2,4,6-Trichlorophenol	CAS-Number: 88–06–2
3,4,5-Trichlorophenol	CAS-Number: 609–19–8
2,3,4,5-Tetrachlorophenol	CAS-Number: 4901–51–3
2,3,4,6-Tetrachlorophenol	CAS-Number: 58–90–2
2,3,5,6-Tetrachlorophenol	CAS-Number: 935–95–5
Pentachlorophenol	CAS-Number: 87–86–5

NOTE This chlorinated phenol mix is available from laboratory chemical suppliers.

6.2 Tetrachloroguaiacol (TCG) (tetrachloro-*o*-methoxyphenol), at a concentration of 100 µg/ml in acetone (internal standard), melting point 118 °C to 119 °C.

6.3 Sulfuric acid, 1 mol/l.

6.4 *n*-hexane, for residue analysis.

6.5 Potassium carbonate, K_2CO_3.

6.6 Acetic anhydride, $C_4H_6O_3$.

6.7 Anhydrous sodium sulphate.

6.8 Distilled water, in accordance with Grade 3 of ISO 3696.

6.9 Triethylamine.

6.10 Acetone.

7 Sampling and preparation of samples

If possible, sample in accordance with ISO 2418. Cut the leather sample into small pieces or grind the leather in accordance with ISO 4044. The dimensions of the pieces shall not be larger than 2 mm to 3 mm. If sampling in accordance with ISO 2418 is not possible (e.g. leathers from finished products like shoes, garments), details about sampling shall be given together with the test report.

8 Procedure

8.1 Steam-distillation

Accurately weigh approximately 1,0 g of the leather sample into the distillation vessel (5.3). Add 20 ml of 1 mol/l sulfuric acid (6.3) and 100 µl of the TCG stock solution (6.2). Submit the contents of the vessel to a steam distillation by using a suitable steam distillation apparatus. Use a 500 ml volumetric flask (5.5) with 5 g K_2CO_3 (6.5) to collect the distillate.

Distill about 450 ml. Make up to volume (500 ml) with distilled water (6.8).

In the case of extreme foaming, the heat source should be reduced.

8.2 Liquid-liquid-extraction and acetylation

8.2.1 Transfer 100 ml of the distillate obtained in 8.1 into a 250 ml separating funnel (5.7).

8.2.2 Add 20 ml *n*-hexane (6.4), 0,5 ml triethylamine (6.9), and 1,5 ml acetic anhydride (6.6) to the solution and shake for 30 min on a mechanical shaker (5.4) with a shaking rate of at least 200 shakes per min.

CAUTION — This step shall be carried out in a well-ventilated area or fume cupboard.

NOTE The derivatization step is a two-phase reaction and depends very strongly on the intensity of shaking. Use a suitable mechanical shaker with a high shaking frequency (at least 200 cycles/min). Do not try to shake by hand because this will produce inconsistent results. Pressure compensation should be carried out before fixing the separating funnel (5.7) to the mechanical shaker (5.4).

8.2.3 After phase separation, transfer the organic layer to a 100 ml conical flask (5.6) and shake the aqueous layer for a further 30 min with an additional 20 ml of *n*-hexane.

8.2.4 Dehydrate the combined *n*-hexane extracts by adding anhydrous sodium sulfate (6.7) to the flask (5.6) and leaving to stand for approximately 10 min.

8.2.5 Filter (5.9) the *n*-hexane extract quantitatively, washing with *n*-hexane into a 50 ml volumetric flask (5.5).

8.2.6 Make up to volume (50 ml) with *n*-hexane.

8.2.7 Analyse this solution by one of the gas chromatographic methods (5.1).

8.3 Preparation of calibration mixture for acetylated CP and TCG

8.3.1 Derivatization of chlorinated phenol mix and TCG standard for recovery rate

To calculate the recovery, prepare a CP/TCG standard mixture like the sample.

Measure 100 µl of the chlorinated phenol mix solution (6.1) and 100 µl TCG (6.2) into the distillation vessel together with 20 ml sulfuric acid (6.3). Treat this solution in the same way as the sample.

The recovery rate shall be higher than 90 %.

8.3.2 Chlorinated phenol mix (external standard)

Acetylate 20 µl of the chlorinated phenol mix solution (6.1) and 20 µl TCG-solution (6.2) in 30 ml of 0,1 mol/l K_2CO_3 in the same way as the sample (8.2.2 – 8.2.7) and transfer the organic layer into a 50 ml volumetric flask (5.5) and fill up to volume with *n*-hexane.

The final concentration for the GC is 0,04 µg/ml per compound.

This standard is included in the calculation.

NOTE This final concentration is suitable for CP concentrations of 5 mg/kg or more in leather. For determining lower concentrations of CP in leather, the final concentration of the external standard should be proportionally reduced.

8.4 Gas chromatography (GC)

Various types of gas chromatographic equipment can be used. The chromatographic conditions given in Annex A are examples of parameters that have been successfully used for this analysis. Annex B gives results for the reliability of the method.

9 Expression of results

Compare the areas of the single peaks with the areas of the standard which are analysed simultaneously and calculated.

Calculate the CP concentration as a mass fraction, w_{CP}, in milligrams per kilogram (mg/kg) of the leather sample, according to the following formula:

$$w_{CP} = \frac{A_{CP-S} \cdot c_{CP-St} \cdot A_{TCG-St} \cdot V \cdot \beta}{A_{CP-St} \cdot A_{TCG-S} \cdot m} \quad (1)$$

where

$A_{CP\text{-}S}$ is the peak area of the sample;

$A_{CP\text{-}St}$ is the peak area of the CP standard;

$A_{TCG\text{-}S}$ is the peak area of the internal standard (TCG) in the sample;

$A_{TCG\text{-}St}$ is the peak area of the internal standard (TCG) in the standard;

c is the concentration of the chlorinated phenol in the calibration standard in micrograms per millilitre, µg/ml (8.3.2);

m is the mass of the sample in grams, g;

V is the final sample volume in millilitres, ml;

β is the dilution factor.

Results based on dry matter:

$$w_{CP-dry} = w_{CP} \cdot D \quad (2)$$

where

D is the factor for conversion to dry matter: $D = 100/(100 - w)$;

w is the volatile matter determined using ISO 4684.

10 Test report

The test report shall include the following information:

a) a reference to this International Standard, i.e. ISO 17070;

b) the type, origin, and designation of the analysed leather sample and the sampling method used;

c) the analytical result for each CP in milligrams per kilogram (mg/kg) rounded to one decimal place;

d) any deviations from the analytical procedure;

e) the date of the test.

Annex A
(informative)

Chromatographic analyses

A.1 Preliminary remark

As the instrumental equipment (5.1) of the laboratories may vary, no generally applicable instructions can be provided for gas chromatographic analyses. The following chromatographic conditions are an example of parameters that have been successfully used for this analysis.

A.2 Gas chromatography with electron capture detector (GC-ECD)

Capillary column:	fused quartz, medium polarity, e.g. 95 % dimethyl-5 % diphenylpolysiloxane, length 50 m; inner diameter: 0,32 mm; film thickness: 0,25 µm;
Detector/detect. temperature:	ECD/280 °C;
Injection system:	split/splitless 60 s;
Injection volume:	2 µl;
Injection temp.:	250 °C;
Carrier gas:	helium;
Make up gas:	argon (95 %)/methane (5 %);
Temperature programme:	80 °C (1 min), 6 °C/min → 280 °C (10 min).

A.3 Gas chromatography with mass selective detector (GC-MSD)

Column:	5 % phenyl methyl siloxane, e.g. DB-5MS or equivalent is suitable, length 30 m; internal diameter: 0,25 mm; film thickness: 0,25 µm;
Injection system:	splitless, time 2 min;
Injection volume:	2 µl;
Injection temp.:	250 °C;
Carrier gas:	helium, flow rate: 1,2 ml/min;
Temperature programme:	60 °C, up to 100 °C at 15 °C/min, up to 220 °C at 8 °C/min, up to 300 °C at 50 °C/min, hold for 1 min.
MS conditions:	Transfer line: 300 °C, Ion source: 230 °C, Quadrupole: 150 °C, solvent delay: 4 min;
MS detection:	see Table A.1

Table A.1 — m/z signals of the chlorinated phenols and SIM time of the groups in minutes

NR.	Substance class	m/z	SIM Time
1	MoCP	128/130	0 - 7,1 min
2	DiCP	162/164/166	7,1 – 9 min
3	TriCP	196/198/200	9 - 11,6 min
4	TeCP	230/232/234	11,6 - 13,8 min
5	PCP	264/266/268	13,8 min - end
6	TCG (internal standard)	260/262/264	13,8 min - end

Annex B
(informative)

Reliability of the method

B.1 Quantification limit for PCP

Only under optimal conditions will the quantification limit given below be possible for PCP. The optimal conditions will especially depend on the GC equipment used and the detector sensitivity.

Quantification limit of PCP: 0,1 mg/kg

NOTE With this method, the determination of quantification limits for other chlorinated phenols is possible, but it should be noted that the quantification limit will be higher for the chlorinated phenols with lower chlorine contents.

B.2 Interlaboratory trial results for PCP

The method in this International Standard has been tested in an interlaboratory collaborative trial using three different leathers (A, B, and C), each containing a different amount of PCP. The results are presented in Table B.1.

Recovery of PCP: 96 % to 107 % (0,09 ppm to 3 ppm)

Recovery of PCP-acetate-standard: 80 %

Table B.1 — Interlaboratory trial results for PCP

Values in milligrams per kilogram (mg/kg)

Leather	Mean	s_r	r	s_R	R
A	6,7	0,4	1,2	0,8	2,3
B	16,8	0,5	1,4	2,1	5,8
C	5,0	0,3	0,9	0,6	1,5

Symbols:

s_r standard deviation of repeatability

r repeatability

s_R standard deviation of reproducibility

R reproducibility

(*Continued from second cover*)

In this adopted standard, reference appears to certain International Standards where the standard atmospheric conditions to be observed are stipulated which are not applicable to tropical/subtropical countries. The applicable standard atmospheric conditions for Indian conditions are 27 °C ± 2 °C and (65 ± 5) percent, relative humidity and shall be observed while using this standard.

In reporting the result of a test or analysis made in accordance with this standard, if the final value, observed or calculated, is to be rounded off, it shall be done in accordance with IS 2 : 2022. 'Rules for rounding off numerical values (*second revision)'*.

Bureau of Indian Standards

BIS is a statutory institution established under the *Bureau of Indian Standards Act*, 2016 to promote harmonious development of the activities of standardization, marking and quality certification of goods and attending to connected matters in the country.

Review of Indian Standards

Amendments are issued to standards as the need arises on the basis of comments. Standards are also reviewed periodically; a standard along with amendments is reaffirmed when such review indicates that no changes are needed; if the review indicates that changes are needed, it is taken up for revision. Users of Indian Standards should ascertain that they are in possession of the latest amendments or edition by referring to the website-www.bis.gov.in or www.standardsbis.in.

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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.gov.in

Regional Offices:		*Telephones*
Central	: 601/A, Konnectus Tower -1, 6th Floor, DMRC Building, Bhavbhuti Marg, New Delhi 110002	2323 7617
Eastern	: 8th Floor, Plot No 7/7 & 7/8, CP Block, Sector V, Salt Lake, Kolkata, West Bengal 700091	2367 0012 2320 9474
Northern	: Plot No. 4-A, Sector 27-B, Madhya Marg, Chandigarh 160019	265 9930
Southern	: C.I.T. Campus, IV Cross Road, Taramani, Chennai 600113	2254 1442 2254 1216
Western	: Manakalya, 4th Floor, NTH Complex (W Sector), F-10, MIDC, Andheri (East), Mumbai 400093	283 25838

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