INTERNATIONAL STANDARD

ISO 11401

First edition
1993-12-01

Plastics — Phenolic resins — Separation by liquid chromatography

Plastiques — Résines phénoliques — Séparation par chromatographie en phase liquide

Reference number
ISO 11401:1993(E)

Foreword

ISO (the International Organization for Standardization) is a worldwide federation of national standards bodies (ISO member bodies). The work of preparing International Standards is normally carried out through ISO technical committees. Each member body interested in a subject for which a technical committee has been established has the right to be represented on that committee. International organizations, governmental and non-governmental, in liaison with ISO, also take part in the work. ISO collaborates closely with the International Electrotechnical Commission (IEC) on all matters of electrotechnical standardization.

Draft International Standards adopted by the technical committees are circulated to the member bodies for voting. Publication as an International Standard requires approval by at least 75 % of the member bodies casting a vote.

International Standard ISO 11401 was prepared by Technical Committee ISO/TC 61, *Plastics*, Sub-Committee SC 12, *Thermosetting materials*.

Later, this International Standard will become part of a general standard concerning liquid chromatography.

International Organization for Standardization
Case Postale 56 • CH-1211 Genève 20 • Switzerland

Printed in Switzerland

INTERNATIONAL STANDARD ISO 11401:1993(E)

Plastics — Phenolic resins — Separation by liquid chromatography

1 Scope

1.1 This International Standard specifies chromatographic methods for the separation of phenolic resins into their component compounds. Separation takes place according to molecular weight and/or polarity.

There are various liquid chromatographic methods:

A: Gel-permeation chromatography

B: High-performance liquid chromatography on polar columns

C: High-performance liquid chromatography on non-polar columns

It is possible to separate a phenolic resin into its components according to molecular size using method A (gel-permeation chromatography). Whereas free phenol and the sum of the dihydroxydiphenylmethanes (in novolaks) and various methylolphenols (in resols) are quantitatively separated in this procedure, high-molecular-weight components of the resins are only incompletely separated due to the multitude of isomers.

Methods B and C (high-performance liquid chromatography) separate the compounds in the resin according to molecular weight *and* polarity. Molecular-weight effects predominate on polar stationary phases (method B), and the effect of polarity on non-polar stationary phases (method C). These methods also allow quantitative determination of individual low-molecular-weight resin components. Because of the different resin solubilities, method B is more suitable for novolaks and method C for resols.

1.2 The methods are applicable to phenolic resins that are soluble in the solvents and solvent blends used.

1.3 This test is useful for characterization of products and for research.

2 Normative references

The following standards contain provisions which, through reference in this text, constitute provisions of this International Standard. At the time of publication, the editions indicated were valid. All standards are subject to revision, and parties to agreements based on this International Standard are encouraged to investigate the possibility of applying the most recent editions of the standards indicated below. Members of IEC and ISO maintain registers of currently valid International Standards.

ISO 472:1988, *Plastics — Vocabulary.*

ISO 10082:1991, *Plastics — Phenolic resins — Definitions and test methods.*

3 Definitions

For the purposes of this International Standard, the following definitions apply.

3.1 phenolic resin: Generally, a class of resins made by the polycondensation of phenol, its homologues and/or derivatives, with aldehydes or ketones. [ISO 472]

3.2 novolaks: Non-self-curing, soluble, fusible phenolic resins that remain stable when stored, the phenol nuclei of which are linked primarily by methylene bridges. Novolaks can be made to react further and crosslink by the addition of hardeners; heating is also usually necessary. [ISO 10082]

See also *novolak* in ISO 472.

3.3 resols: Soluble, fusible phenolic resins which, in contrast to novolaks, contain methylol groups and methylene-ether and sometimes also methylene-amine bridges. Resols are self-curing; they crosslink into insoluble products when heated and/or mixed with catalysts, without addition of further reaction components. Resols are perishable and can be stored for a limited time only. [ISO 10082]

See also *resol* in ISO 472.

4 Test methods

4.1 Method A — Gel-permeation chromatography

NOTE 1 The reagents, apparatus and test conditions given are examples. Others may be used if similar or better results are obtained.

4.1.1 Principle

A test sample of the phenolic resin is dissolved in a suitable solvent and the molecular-weight distribution is determined by separation on columns with polymer gels having different pore diameters.

4.1.2 Reagents

4.1.2.1 Tetrahydrofuran, chromatography grade.

4.1.3 Apparatus

4.1.3.1 Pump, with sample inlet and adjustable, surge-free throughput.

4.1.3.2 UV detector or **refractometer**.

4.1.3.3 Printer/plotter.

4.1.3.4 Integrator or **computer**.

4.1.3.5 Gel-chromatography separation column system, such as

2 × 100 Å, 600 mm × ⌀ 7,7mm

2 × 1 000 Å, 600 mm × ⌀ 7,7 mm

4.1.3.6 Automatic sampler (optional).

4.1.4 Preparation of test sample

4.1.4.1 Since only small quantities of materials are used, it is essential that test samples be representative of the material.

4.1.4.2 For injection, a 100 mg sample of the material is dissolved in 10 ml of tetrahydrofuran (4.1.2.1).

4.1.5 Test conditions

Temperature: room temperature

Carrier: tetrahydrofuran

Flow rate: 1 ml/min

Injection volume: 20 µl

Detector: UV detector at 254 nm or 280 nm, or refractometer

4.1.6 Evaluation of results

Exact calibration for determination of the molecular-weight distribution is difficult since the phenolic hydroxyl groups add to tetrahydrofuran, although this addition is incomplete in long-chain molecules due to steric hindrance.

Qualitative evaluation may be carried out by comparison of chromatograms. If a computer with appropriate software is available, chromatograms can be subtracted from one another to emphasize differences in the degree of condensation and the molecular-weight distribution.

With good separation, some low-molecular-weight components (phenol, methylolphenols and the sum of dihydroxydiphenylmethanes) may also be determined quantitatively (see 4.3.8).

4.1.7 Sample chromatogram of a phenolic novolak

See figure 1.

4.2 Method B — High-performance liquid chromatography on polar columns

See 4.1, note 1.

4.2.1 Principle

A test sample of the phenolic resin is dissolved in a suitable solvent and separated on the polar column. The carrier is a solvent blend run with a concentration gradient. Novolaks and tetrahydrofuran-soluble resols may be analysed.

4.2.2 Reagents

4.2.2.1 Tetrahydrofuran, chromatography grade.

4.2.2.2 Heptane, chromatography grade.

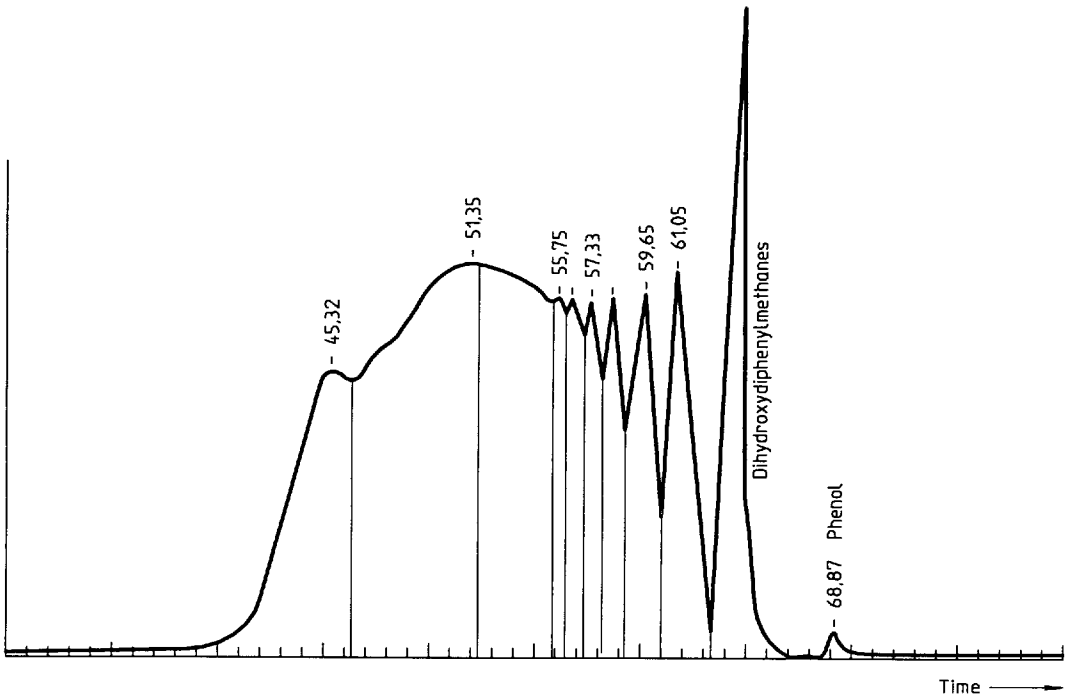

Figure 1 — Example of a phenol novolak chromatogram

4.2.3 Apparatus

4.2.3.1 Pump, with sample inlet and adjustable, surge-free throughput.

4.2.3.2 UV detector.

4.2.3.3 Printer/plotter.

4.2.3.4 Integrator or **computer**.

4.2.3.5 Column for polar chromatography, such as a 125 mm × Ø 4 mm column packed with 5 µm silica gel.

4.2.3.6 Automatic sampler (optional).

4.2.4 Preparation of test sample

4.2.4.1 Since only small quantities of materials are used, it is essential that test samples be representative of the material.

4.2.4.2 For injection, a 100 mg sample of the material is dissolved in 10 ml of tetrahydrofuran (4.2.2.1).

4.2.5 Test conditions

Temperature: room temperature

Carrier: tetrahydrofuran-heptane

Time	THF	Heptane
(min)	(%)	(%)
0	25	75
10	50	50
40	100	0
44	100	0
47	25	75
55	25	75

Flow rate: 0,5 ml/min

Injection volume: 20 µl

Detector: UV detector at 254 nm or 280 nm

4.2.6 Evaluation of results

Qualitative evaluation is carried out by comparison of chromatograms.

With good separation, some low-molecular-weight components (phenol, dihydroxydiphenylmethanes and

phenolic alcohols) may also be determined quantitatively (see 4.3.8).

4.2.7 Sample chromatogram of a phenolic novolak on a polar column

See figure 2.

4.3 Method C — High-performance liquid chromatography on non-polar (reversed-phase) columns

See 4.1, note 1.

4.3.1 Principle

A test sample of the phenolic resin is dissolved in a suitable solvent and separated on the non-polar column. The carrier is a solvent blend run with a concentration gradient.

4.3.2 Reagents

4.3.2.1 Water, chromatography grade.

4.3.2.2 Methanol, chromatography grade.

4.3.2.3 Tetrahydrofuran, chromatography grade.

4.3.3 Apparatus

4.3.3.1 Pump, with sample inlet and adjustable, surge-free throughput.

4.3.3.2 UV detector.

4.3.3.3 Printer/plotter.

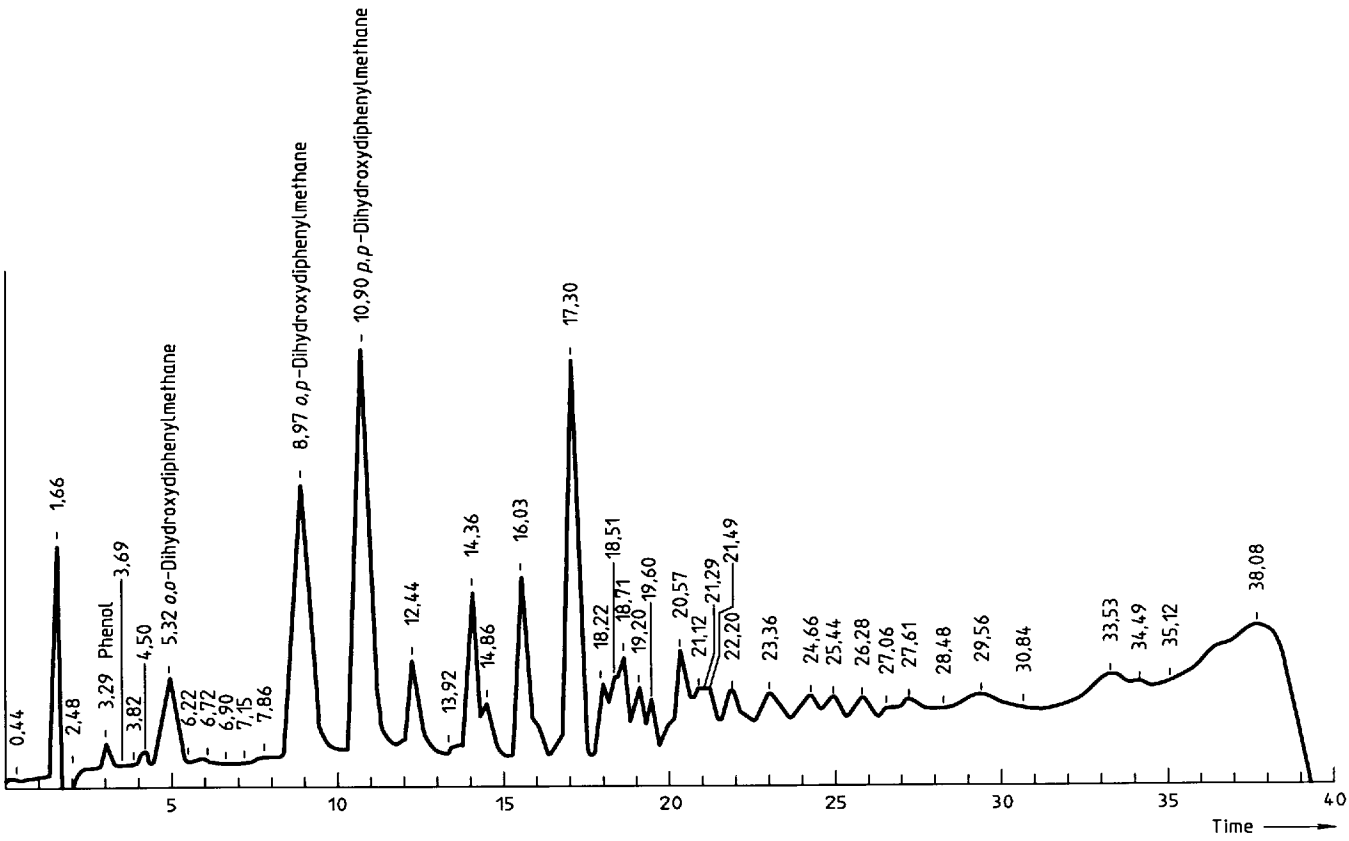

Figure 2 — Example of a phenol novolak chromatogram produced using a polar column

4.3.3.4 Integrator or **computer**.

4.3.3.5 Column for non-polar chromatography, such as a 125 mm × ⌀ 4 mm column packed with 5 µm RP 18.

4.3.3.6 Automatic sampler (optional).

4.3.4 Preparation of test sample

4.3.4.1 Since only small quantities of materials are used, it is essential that test samples be representative of the material.

4.3.4.2 The following pretreatments may be used with resols;

a) alkaline resol samples can be neutralized with formic acid to convert phenates to phenols;

b) ammonium hydroxide can be added to resols to destroy the oxymethylene chaining that occurs at each methylol end group.

4.3.4.3 For injection, a 100 mg sample of the material is dissolved in 10 ml of tetrahydrofuran (4.3.2.3).

4.3.5 Test conditions

Temperature: room temperature

Carrier: methanol-water

Time (min)	Methanol (%)	Water (%)
0	10	90
7	30	70
15	45	55
35	95	5
38	95	5
48	10	90
60	10	90

Flow rate: 0,5 ml/min

Injection volume: 20 µl

Detector: UV detector at 254 nm or 280 nm

4.3.6 Evaluation of results

Qualitative evaluation is carried out by comparison of chromatograms.

Quantitative determination of individual components in phenolic resins using an internal standard is difficult with non-polar chromatography, since the intervals between individual peaks are too small. It may be done with external standards (see 4.3.8).

4.3.7 Sample chromatogram of a phenolic resol on a non-polar column

See figure 3.

4.3.8 Quantitative evaluation with an internal or external standard

The internal or external factor for the component to be determined must be established first. This requires the component to be available in pure form. In the case of an external standard, the component to be determined shall be used.

The factor f for an internal standard is calculated using the formula:

$$f = \frac{A_S m_C}{m_S A_C}$$

where

A_C is the peak area for the component concerned;

A_S is the peak area for the internal standard;

m_C is the mass of the component concerned;

m_S is the mass of the internal standard.

The fraction w_C of the component, expressed as a percentage by mass, in the resin is then calculated using the formula:

$$w_C = \frac{A_C f m_S}{m A_S} \times 100$$

where

m is the mass of the test sample;

A_C, A_S, f and m_S are as defined above.

When using an external standard, a calibration curve shall be established.

5 Test report

The test report shall include the following information:

a) a reference to this International Standard;

b) all details necessary for the complete identification of the phenolic resin tested;

c) the method used (method A, B or C);

d) the columns and stationary phases used;

e) the apparatus delay and retention volumes;

f) the carrier-solvents used and their concentration gradients;

g) any conditions deviating from those specified;

h) a copy of the chromatogram obtained;

i) the results of any quantitative determinations performed;

j) the external or internal standard used;

k) the date of the test.

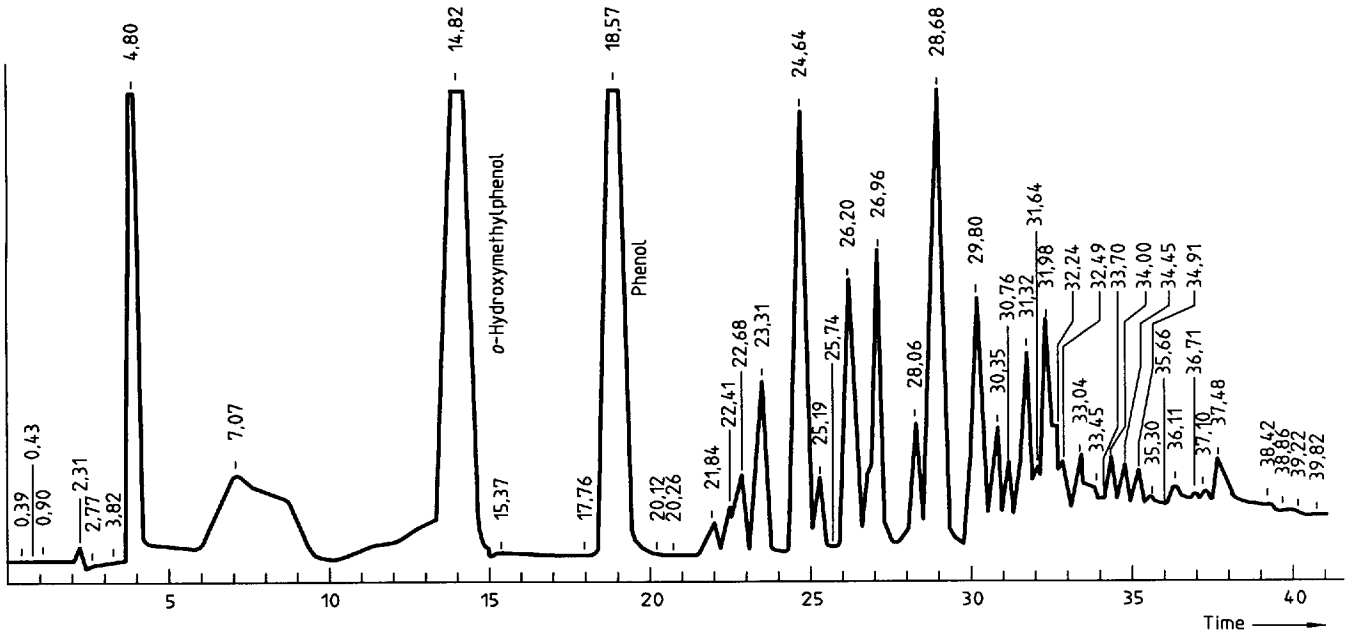

Figure 3 — Example of a phenol resol chromatogram produced using a non-polar column

UDC 678.632.01:543.544

Descriptors: plastics, thermosetting resins, phenoplasts, tests, determination of content, separation methods, chromatography, high performance liquid chromatography.

Price based on 6 pages