International
Standard

ISO 19403-4

Second edition
2024-10

Paints and varnishes — Wettability —

Part 4:
Determination of the polar and dispersive fractions of the surface tension of liquids from an interfacial tension

Peintures et vernis — Mouillabilité —

Partie 4: Détermination des fractions polaire et dispersive de la tension superficielle des liquides à partir d'une tension interfaciale

Reference number
ISO 19403-4:2024(en)

ISO copyright office
CP 401 • Ch. de Blandonnet 8
CH-1214 Vernier, Geneva
Phone: +41 22 749 01 11
Email: copyright@iso.org
Website: www.iso.org

Published in Switzerland

Contents

Page

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.

The procedures used to develop this document and those intended for its further maintenance are described in the ISO/IEC Directives, Part 1. In particular, the different approval criteria needed for the different types of ISO document should be noted. This document was drafted in accordance with the editorial rules of the ISO/IEC Directives, Part 2 (see www.iso.org/directives).

ISO draws attention to the possibility that the implementation of this document may involve the use of (a) patent(s). ISO takes no position concerning the evidence, validity or applicability of any claimed patent rights in respect thereof. As of the date of publication of this document, ISO had not received notice of (a) patent(s) which may be required to implement this document. However, implementers are cautioned that this may not represent the latest information, which may be obtained from the patent database available at www.iso.org/patents. ISO shall not be held responsible for identifying any or all such patent rights.

Any trade name used in this document is information given for the convenience of users and does not constitute an endorsement.

For an explanation of the voluntary nature of standards, the meaning of ISO specific terms and expressions related to conformity assessment, as well as information about ISO's adherence to the World Trade Organization (WTO) principles in the Technical Barriers to Trade (TBT), see www.iso.org/iso/foreword.html.

This document was prepared by Technical Committee ISO/TC 35, *Paints and varnishes*, Subcommittee SC 9, *General test methods for paints and varnishes*, in collaboration with the European Committee for Standardization (CEN) Technical Committee CEN/TC 139, *Paints and varnishes*, in accordance with the Agreement on technical cooperation between ISO and CEN (Vienna Agreement).

This second edition cancels and replaces the first edition (ISO 19403-4:2017), which has been technically revised.

The main changes are as follows:

- in 5.3, the requirement on the wall thickness of the optical cell has been reduced to 2 mm;
- in 5.4, the requirement for the reference liquids has been changed from colourless to transparent;
- the normative references have been updated.

A list of all parts in the ISO 19403 series can be found on the ISO website.

Any feedback or questions on this document should be directed to the user’s national standards body. A complete listing of these bodies can be found at www.iso.org/members.html.

Paints and varnishes — Wettability —

Part 4:
Determination of the polar and dispersive fractions of the surface tension of liquids from an interfacial tension

1 Scope

This document specifies a test method to determine the polar and dispersive fractions of the surface tension of liquids from an interfacial tension with optical methods. The method can be applied for the characterization of liquid coating materials, especially if drying effects occur during alternative measurement. If applied to liquids with non-Newtonian flow behaviour (see ISO 3219-1:2021, 3.22), restrictions can apply.

2 Normative references

The following documents are referred to in the text in such a way that some or all of their content constitutes requirements of this document. For dated references, only the edition cited applies. For undated references, the latest edition of the referenced document (including any amendments) applies.

ISO 1409, *Plastics/rubber — Polymer dispersions and rubber latices (natural and synthetic) — Determination of surface tension*

ISO 4618, *Paints and varnishes — Vocabulary*

ISO 15528, *Paints, varnishes and raw materials for paints and varnishes — Sampling*

ISO 19403-1, *Paints and varnishes — Wettability — Part 1: Vocabulary and general principles*

ISO 19403-3, *Paints and varnishes — Wettability — Part 3: Determination of the surface tension of liquids using the pendant drop method*

EN 14370, *Surface active agents — Determination of surface tension*

3 Terms and definitions

For the purposes of this document, the terms and definitions given in ISO 4618 and ISO 19403-1 apply.

ISO and IEC maintain terminology databases for use in standardization at the following addresses:

- ISO Online browsing platform: available at https://www.iso.org/obp
- IEC Electropedia: available at https://www.electropedia.org/

4 Principle

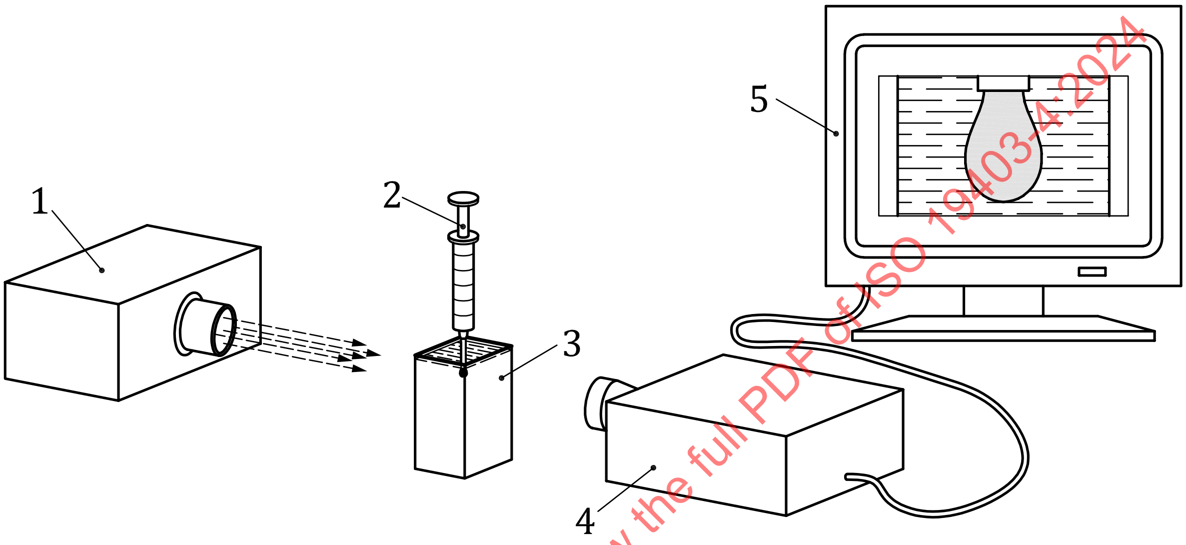
One drop of the respective liquid to be tested, hanging from or ascending from a needle, is reproduced within an optical cell, which is completely filled with a reference liquid. The reproduced drop shall deviate significantly from the spherical shape due to the difference in density compared to the reference liquid. The interfacial tension is calculated from the shape of the reproduced pendant or ascending drop according to the Young-Laplace equation (see ISO 19403-1:2022, 3.2.2). The polar and dispersive fraction of the surface tension of the liquid to be tested can be determined from the obtained interfacial tension and the known surface tensions of both the liquid to be tested and the reference liquid.

5 Apparatus and materials

Ordinary laboratory apparatus, together with the following, shall be used.

5.1 Drop contour analysis system, for measurement of the surface tension of pendant drops.

Any state-of-the-art drop contour analysis system with digital image capture and analysis can be used. Figure 1 and Figure 2 show a schematic example of a drop contour analysis system.



Key

1 light source

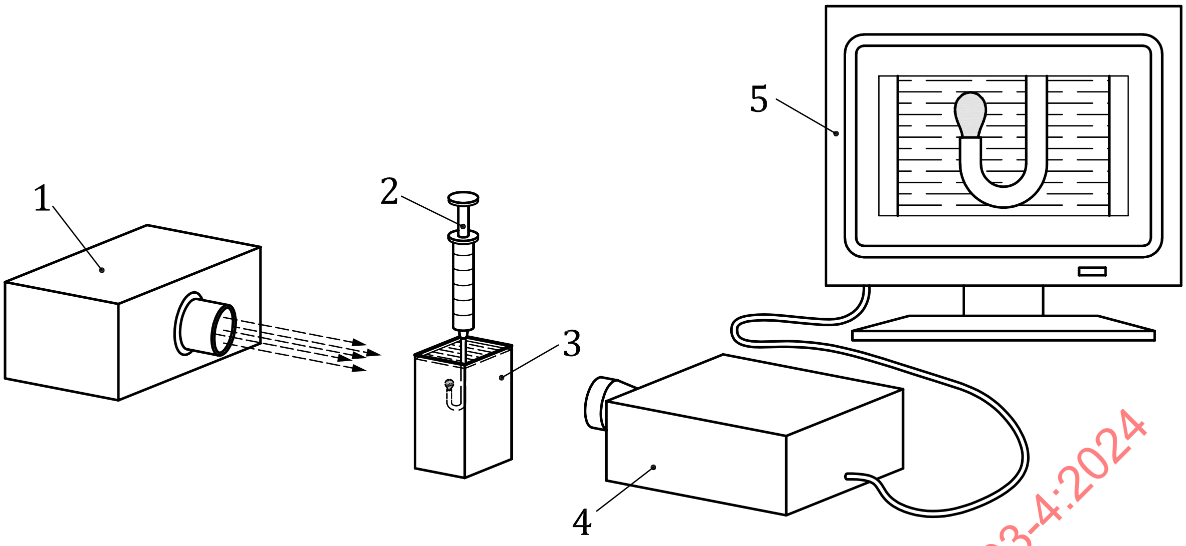
2 dosing unit with graduated microsyringe

3 optical cell

4 image taking and analysing unit

5 screen

Figure 1 — Drop contour analysis system with pendant drop



Key

1	light source
2	dosing unit with graduated microsyringe
3	optical cell
4	image taking and analysing unit
5	screen

Figure 2 — Drop contour analysis system with ascending drop

The image taking system should be oriented in a way that the optimal image resolution ratio (ratio of width and height) can be used.

NOTE The device used can differ from the schematic diagram in regard to light path and the set-up of the components.

5.2 Dosing unit, which makes it possible to dose a pendant liquid drop, which deviates significantly from the spherical shape due to its own mass, on a circular-cylindrical needle with constant wall thickness within the detection area of the camera.

The needle used can be straight or bent in a J-shape.

J-shaped needles, whose free end points upwards, are necessary when the density of the liquid to be tested is lower than the density of the reference liquid.

For the measurement of the surface tension on the pendant or ascending drop, usually a larger outside diameter of the needle is required than for the measurement of the contact angle on the horizontal drop. The outside diameters of the needles used shall be in the range between 0,5 mm and 2,5 mm. The ideal outside diameter of the needle depends on the relationship between the interfacial tension, σ_{LR}, and the density difference, $\Delta\rho_{lr} = \rho_l - \rho_r$, of the liquid to be tested, ρ_l, and the reference liquid, ρ_r. The higher the quotient, $\sigma_{lr}/\Delta\rho_{lr}$, the larger the outside diameter of the needle should be.

5.3 Optical cell, with plane and side walls running parallel to each other. Through these sides which are made of optically impeccable clear-transparent materials (e.g. made of glass or insoluble, optically useable plastic), the observation of the formed drop is carried out in a way so that a representation without optical errors is possible. In addition, the inner and outer walls of the optical cell shall be free of contaminations (e.g. finger prints, adhering particles and surfactants). The wall thickness of the optical cell should be less than 2 mm. Otherwise, apparent drop size can change due to refraction of light.

5.4 Reference liquids, which shall not be miscible and shall be able to form a meniscus. Reference liquids shall be chemically homogenous, strictly dispersive and transparent with a melting point lower than 20 °C.

Preferably, liquid hydrocarbons or perfluorohydrocarbons (e.g. *n*-perfluorohexane and *n*-perfluorooctane) free from polar contaminations can be used. Among the hydrocarbons, especially *n*-decane, *n*-dodecane, *n*-tetradecane and *n*-hexadecane are suitable as reference liquids.

NOTE 1 Perfluorohydrocarbons can be prohibited in some countries.

NOTE 2 The viscosity of the mentioned reference liquids at 23 °C is in the range of that of water. This is of advantage for the setting of the equilibrium.

6 Sampling

Take a representative sample of the liquid to be tested in accordance with ISO 15528.

7 Procedure

7.1 Preparation for the procedure

7.1.1 Setting up the drop contour analysis device

Choose the location of the drop contour analysis device, so that it is not exposed to:

- vibrations,
- intense air flows (e.g. caused by air conditioning), and
- intense exposure to light from outside (e.g. windows, bright lighting).

Align the drop contour analysis device horizontally.

7.1.2 Test conditions

Carry out the test at (23 ± 2) °C (see ISO 3270) and ensure that all test media have this temperature.

7.1.3 Cleaning and conditioning of the reference liquid

The measurable interfacial tension compared to water shall be at least 52 mN/m at 23 °C after the cleaning of the recommended *n*-alkanes (see 5.4).[5]

The residual content of ketones in the *n*-alkanes can be removed by the following cleaning procedure. The cleaning of the hydrocarbons used as reference liquids can be carried out in chromatography columns with a minimum length of 60 cm, which are filled with silica gel (e.g. particle size mesh 60). The silica gel used shall have polar surfaces in order to sufficiently absorb the polar contaminations that originate from the production process during passing through the hydrocarbons. Cleaning by distillation is also possible.

The cleaned *n*-alkanes shall be stored in light-proof glass bottles in the refrigerator at a maximum temperature of 4 °C.

It is not necessary to clean perfluorohydrocarbons beforehand, since after the normal industrial production process (electrofluorination) of these liquids, no measurable content of polar contaminations is expected. An interfacial tension compared to water at 23 °C for the recommended perfluoroalkanes (*n*-perfluorohexane and *n*-perfluorooctane) of at least 54 mN/m at 23 °C should be observed.[6]

7.2 Determination of the interfacial tension of the liquid

7.2.1 Preparations

In case it is not given, obtain the density of the liquid to be tested as well as the density of the reference liquid and calculate the density difference.

Fill the optical cell with the reference liquid to about 80 %.

Determine the outside diameter of the needle to ±0,005 mm. This can be done using a microscope or a micrometer according to ISO 2808.

It shall be considered that especially in the case of J-shaped dosing needles, the end of the needle runs out circular-cylindrical.

Fill the dosing system with the liquid to be tested. Pay attention to fill without contamination and bubbles.

Move the needle to the upper margin of the image in case of a pendant drop or to the lower margin of the image in case of an ascending drop and bring the edges of the needle into focus. Set up the zoom of the drop contour analysis device so that the diameter of the needle takes up at least one eighth of the width of the image. Refocus if necessary.

7.2.2 Procedure

Produce a preferably large pendant or ascending drop within the optical cell. The drop shall touch neither the boundaries of the optical cell nor the meniscus of the ambient liquid phase in the upper area of the optical cell.

In order to avoid interferences of the pendant or ascending drop, as well as image blurring due to convection currents, equilibrium in the optical cell shall be achieved before taking any further steps. To achieve complete equilibrium for the interfacial tension, additional waiting time can be necessary depending on the viscosity and solubility of the liquid to be tested. The exact time until (thermodynamic) equilibrium depends on the size of the optical cell, the ambient thermostatic control and the properties of the liquids themselves.

If the single parts of the liquid to be tested dissolve in the reference liquid, the reference liquid shall be changed. In this case, perfluoroalkanes can be used as reference. A further possibility is using the measurement on dispersive reference surfaces (see ISO 19403-5).

After final focusing/zooming, carry out a length calibration of the imaging device. Update the lighting, if necessary.

Do not change the zoom and focus after this determination of scale.

Take an image of the pendant or ascending drop.

For traceability reasons, the original image should be saved.

Repeat measurement on at least two more drops. Calculate the mean value and the standard deviation of the interfacial tension from all single measurement values.

7.3 Determination of the surface tension of liquids

Measure the surface tension of the liquid to be tested, as well as the surface tension of the reference liquid in accordance with ISO 19403-3, EN 14370 or ISO 1409.

8 Evaluation

8.1 General

The value of the surface tension for each liquid is calculated as the arithmetic mean value of the measurement values. The value of the interfacial tension between the two liquids is also calculated as arithmetic mean value of the measurement values.

The relative standard deviations should not exceed the following values:

- for the surface tension of the tested liquid: ±1 %;
- for the surface tension of the reference liquid: ±0,5 %;

— for the interfacial tension of the tested liquid compared to the reference liquid: ±1 %.

For the calculation of the dispersive and polar fractions of the surface tension, the Owens-Wendt-Rabel-Kaelble[7],[8],[9] method is used preferably. In case negative polar fractions are calculated, it is recommended to use the Wu method.

8.2 Calculation of the dispersive fraction of the surface tension in accordance with Owens-Wendt-Rabel-Kaelble

Calculate the dispersive fraction of the surface tension of the liquid, $\sigma_\mathrm{l}^\mathrm{d}$, in accordance with Formula (1):

$$\sigma_\mathrm{l}^\mathrm{d} = \frac{(\sigma_\mathrm{l} + \sigma_\mathrm{r} - \sigma_\mathrm{lr})^2}{4\sigma_\mathrm{r}} \tag{1}$$

where

σ_lr is the mean value of the measured interfacial tension between the liquid to be tested and the reference liquid;

σ_l is the surface tension of the tested liquid, measured in accordance with 7.3;

σ_r is the surface tension of the reference liquid, measured in accordance with 7.3.

8.3 Calculation of the dispersive fraction of the surface tension in accordance with Wu

Calculate the dispersive fraction of the surface tension of the liquid, $\sigma_\mathrm{l}^\mathrm{d}$, in accordance with Formulae (2) and (3):

$$\sigma_\mathrm{l} + \sigma_\mathrm{r} - \sigma_\mathrm{lr} = 4\left(\frac{\sigma_\mathrm{r} \cdot \sigma_\mathrm{l}^\mathrm{d}}{\sigma_\mathrm{r} + \sigma_\mathrm{l}^\mathrm{d}}\right) \tag{2}$$

By rewriting, it is received:

$$\sigma_\mathrm{l}^\mathrm{d} = \frac{\sigma_\mathrm{r}(\sigma_\mathrm{l} + \sigma_\mathrm{r} - \sigma_\mathrm{lr})}{3\sigma_\mathrm{r} + \sigma_\mathrm{lr} - \sigma_\mathrm{l}}. \tag{3}$$

8.4 Calculation of the polar fraction of the surface tension of the liquid

Calculate the polar fraction of the surface tension of the liquid, $\sigma_\mathrm{l}^\mathrm{p}$, in accordance with Formula (4):

$$\sigma_\mathrm{l}^\mathrm{p} = \sigma_\mathrm{l} - \sigma_\mathrm{l}^\mathrm{d}. \tag{4}$$

9 Test report

The test report shall contain at least the following information:

a) all details necessary to identify the tested product;

b) a reference to this document, i.e. ISO 19403-4:2024;

c) for the determination of the surface tension of the reference liquid and the liquid to be tested respectively:

    1) the reproduction scale for each drop,

    2) the fit error (deviation of the drop contour from the calculated drop contour),

   3) the amount of drops,
   4) the result of the measurement of the surface tension (arithmetic mean value and standard deviation);

d) for the determination of the polar and dispersive fractions of the surface tension of the liquid:
   1) the result of the measurement of the interfacial tension (arithmetic mean value and standard deviation),
   2) the result of the calculation of the polar and dispersive fraction of the surface tension of the liquid,
   3) the density difference,
   4) the information on whether the polar and disperse fraction was calculated with Owens-Wendt-Rabel-Kaelble or Wu (see 8.2 and 8.3);

e) the random error of the surface tension of the reference liquid as well as the calculated values of the polar and dispersive fractions of the surface tension of the liquid;

f) any deviations from the specified method and their possible influences on the results;

g) any unusual observations during the test;

h) the type of device;

i) the name of the person conducting the test;

j) the date of the test.