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Dyestuffs — Determination of solubility in organic solvents — Gravimetric and photometric methods

Colorants — Détermination de la solubilité dans les solvants organiques — Méthodes gravimétrique et photométrique

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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.

International Standards are drafted in accordance with the rules given in the ISO/IEC Directives, Part 2.

The main task of technical committees is to prepare International Standards. 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.

Attention is drawn to the possibility that some of the elements of this document may be the subject of patent rights. ISO shall not be held responsible for identifying any or all such patent rights.

ISO 7579 was prepared by Technical Committee ISO/TC 35, *Paints and varnishes*, Subcommittee SC 2, *Pigments and extenders*.

This second edition cancels and replaces the first edition (ISO 7579:1990), in which the mixing time has been reduced from 24 h to 3 h but the temperature has been increased from 105 °C to 150 °C, Method B and Annex B have been deleted and a photometric test method has been added.

Introduction

Many dyestuffs are soluble in a solvent to an extent which is independent of the amount of dyestuff present in the solvent, as long as excess dyestuff is present. This concentration is defined as the saturation concentration and represents the solubility of the dyestuff in the solvent. In some cases, however, there is no fixed saturation concentration and the amount of dyestuff which dissolves increases with the amount of dyestuff added. A gravimetric and a photometric procedure to assess the solubility of these dyes are described in this International Standard.

Dyestuffs — Determination of solubility in organic solvents — Gravimetric and photometric methods

1 Scope

This International Standard specifies two methods for determining the solubility of dyestuffs in organic solvents. They are applicable to dyestuffs that do not change chemically under the influence of the solvent and are stable and non-volatile under the specified drying conditions. For volatile solvents (boiling point < 120 °C), the gravimetric procedure is recommended and, for less volatile solvents (boiling point > 120 °C), the photometric procedure is recommended. The choice of procedure should be made on a case-by-case basis.

The methods are suitable for concentrations between 1 g and 1 000 g of dyestuff per litre of solvent. Higher concentrations can be used provided the viscosity of the solution is such that the procedure can be carried out readily.

The methods are not suitable for the determination of insoluble matter in a dyestuff.

2 Normative references

The following referenced documents are indispensable for the application 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 787-2, *General methods of test for pigments and extenders — Part 2: Determination of matter volatile at 105 °C*

ISO 2811-1, *Paints and varnishes — Determination of density — Part 1: Pyknometer method*

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

3 Terms and definitions

For the purposes of this document, the following terms and definitions apply.

3.1
solubility
maximum mass of a dyestuff that is soluble in a given volume of a particular solvent under specified conditions

NOTE Solubility is expressed in grams per litre of solvent (see Annex A). No distinction is made between “true” solubility and “colloidal” solubility.

4 Principle

Different amounts of the dyestuff are each dispersed in a defined volume of a solvent at 23 °C. After mixing for 3 h, each dispersion is centrifuged and the solids content of the supernatant liquid is determined by either gravimetric or photometric measurements.

When using the gravimetric procedure, the amount of dyestuff which dissolves is assessed by determination of the non-volatile-matter content of the solution.

When using the photometric procedure, the amount of dyestuff which dissolves is assessed by determination of the light absorbance compared to that of a standard solution.

5 Solvent

When using the gravimetric procedure, the organic solvent used shall be completely volatile at a temperature below the temperature of decomposition of the dyestuff. The density of the solvent at 23 °C shall be known. The density of the solvent can be determined by the method described in ISO 2811-1 at 23 °C using a glass pyknometer. The dyestuff shall not react chemically with the solvent.

As organic solvents are normally not chemically pure, the grade of purity (including the type and quantity of any major secondary constituents) shall be given in the test report.

With solvents having a boiling point above 120 °C, the photometric method is recommended.

6 Apparatus

Ordinary laboratory apparatus and glassware, together with the following:

6.1 **Balance**, accurate to 0,000 1 g.

6.2 **Weighing bottles**, squat form, with stoppers.

6.3 **Containers**, cylindrical, of capacity about 50 ml, of inert material, with tightly fitting lids.

6.4 **Pipette**, capacity 20 ml (tolerance: ± 0,03 ml).

6.5 **Volumetric flask**, capacity 100 ml (tolerance: ± 0,5 ml).

6.6 **Injection syringes**, capacity 2 ml and 5 ml.

6.7 **Mechanical shaker**, with speed control and, preferably, a cooling unit.

6.8 **Laboratory centrifuge**, capable of imparting a relative centrifugal acceleration of about 10 km/s^2. A centrifuge with a rotational frequency of 2 000 min^{-1} to 3 000 min^{-1} is suitable.

6.9 **Centrifuge tubes**, of transparent and inert material, with tightly fitting lids.

6.10 **Drying oven**, with air circulation and temperature control up to 150 °C (tolerance ± 2 °C).

6.11 **Spectrophotometer**.

6.12 **Ultrasonic bath**.

7 Sampling

Take a representative sample of the product to be tested, as described in ISO 15528.

8 Procedure

8.1 Preliminary determination

If the approximate solubility of the dyestuff in the solvent is not known, carry out a preliminary determination, using the procedure described in 8.2.2 and 8.2.3, with one of the following series of test portions of the dyestuff:

- dyestuff of low solubility: 1 g, 10 g and 50 g of dyestuff per litre of solvent;

- dyestuff of high solubility: 100 g, 500 g and 1 000 g of dyestuff per litre of solvent.

Take as the approximate solubility of the dyestuff the concentration of the dispersion in which the undissolved matter after centrifuging is greater than about one-quarter of the total quantity of dyestuff dispersed.

8.2 Preparation of test solutions

8.2.1 When the approximate solubility of the dyestuff is known or has been determined in the preliminary determination, carry out the following procedure.

Prepare six suspensions by taking test portions of the dyestuff to give concentrations of about 40 %, 60 %, 80 %, 100 %, 120 % and 140 % (by mass) of the approximate solubility, using the procedure described in 8.2.2 and 8.2.3. If, at the lowest concentration employed, 10 % or more of the dyestuff remains undissolved, reduce the concentration until more than 90 % of the dyestuff is dissolved. If, at the highest concentration, the residue is less than 25 % of the test portion, then increase the mass of the test portion.

If the solubility limit cannot be obtained because of a large increase in viscosity with increasing amount of the test portion, the last value obtained shall be recorded (see Clause A.4.)

8.2.2 Place the required amount of dyestuff in a container (6.3) and add exactly 20 ml of the solvent, using the pipette (6.4). Close the container immediately to prevent loss of solvent.

Shake the container using a mechanical shaker (6.7) at (23 ± 2) °C for 3 h. Check that no significant agglomerates are visible. If an orbital shaker is used, this shall be stated in the test report.

8.2.3 After shaking the dyestuff and solvent for 3 h, place portions of the suspension in centrifuge tubes (6.9) and cap each tube. Centrifuge the tubes at (23 ± 2) °C for 10 min. Check whether the supernatant liquid is clear, for instance by observing whether the supernatant liquid flows smoothly from a pipette tube dipped into it; if not, or if in doubt, centrifuge for another 10 min. Decant the supernatant liquid from each tube into a clean, dry container (6.3) and close securely.

8.3 Gravimetric determination of the concentration of the dissolved dyestuff

8.3.1 General

Take a known amount of the supernatant liquid prepared in 8.2.3 and determine the concentration of the dyestuff using the method described in 8.3.2. Carry out the weighings to the nearest 0,2 mg.

For each determination, the amount of supernatant liquid taken shall contain at least 30 mg of the dyestuff.

Two determinations on each supernatant liquid shall be carried out. The mean values shall be recorded and used for the calculation as given in 8.3.4.

8.3.2 Procedure

Place a portion (about 3 g) of the clear supernatant liquid into a previously tared weighing bottle (6.2), insert the stopper and weigh (m_0). Remove the stopper, place the weighing bottle in the oven (6.10) maintained at a temperature about 10 °C below the boiling point of the solvent and leave in the oven until most of the solvent has evaporated (this will normally take about 1 h).

Increase the drying temperature to about 30 °C below the decomposition temperature of the dyestuff and continue drying for a further 3 h.

NOTE Most metal-complex dyestuffs can be dried at a temperature of 150 °C.

If the drying temperature is not at least 50 °C above the boiling point of the solvent, either extend the drying time or remove the last traces of solvent in a vacuum oven. In such cases, there shall, however, be no loss of dyestuff by sublimation.

On completion of drying, place the weighing bottle, together with its stopper, in a desiccator and, after cooling, reweigh the bottle with its stopper inserted.

If the procedure is being carried out for the first time on a particular dyestuff/solvent combination, check that the dyestuff really has dried to constant mass by repeating the drying/weighing operations a second time. If the difference between the first and second weighings is 0,2 mg or less, then it can be assumed that the drying procedure gives constant mass. With subsequent samples of the same kind, the verified drying conditions can be used without the need for further checks.

8.3.3 Determination of non-volatile-matter content of the dyestuff

Use the procedure described in ISO 787-2, carrying out the drying at the temperature which has been demonstrated to give constant mass (see 8.3.2), and express the non-volatile-matter content as the ratio of the mass, in grams, of the residue to the mass, in grams, of the test portion, i.e. as a decimal value less than 1.

8.3.4 Expression of results

The calculation of the solubility of a dyestuff depends on the behaviour of the dyestuff in the particular solvent. If a saturation concentration is obtained, the solubility is determined directly from that concentration (see Clause A.1). If the solubility is dependent on the proportion of dyestuff added, a definite saturation concentration is not obtained and, in this case, the solubility is calculated in accordance with Clause A.2 or is recorded together with the proportion of the dyestuff added (see Clause A.3).

Calculate the solubility S, in grams per litre, of the dyestuff for each test suspension with which settled matter is observed in the centrifuge tubes in 8.2.3, using the following equation:

$$S = \frac{m_1 \cdot \rho}{(m_0 - m_1) \cdot \mathrm{NV}} \qquad (1)$$

where

m_0 is the mass, in grams, of the supernatant liquid taken in 8.3.2;

m_1 is the mass, in grams, of the dry residue obtained in 8.3.2;

ρ is the density, in grams per litre, of the solvent at 23 °C;

NV is the non-volatile-matter content of the dyestuff (see 8.3.3).

Record the solubility as follows:

below 1 g/l:	< 1 g/l;
from 1 g/l to 10 g/l:	the result to the nearest 0,1 g/l;

above 10 g/l up to 1 000 g/l: the result to the nearest 1 g/l;

above 1 000 g/l: > 1 000 g/l.

8.3.5 Precision

No precision data are currently available.

The precision of the method depends very much on the properties of the dyestuff and the solvent. This shall be considered when interpreting the results. Collaborative tests have shown that, in the case of a dyestuff exhibiting a definite saturation concentration (see Clause A.1), a repeatability within ± 5 % is obtained. In the cases described in Clause A.2 and Clause A.3, the repeatability may well be poorer.

8.4 Photometric determination of the concentration of the dissolved dyestuff

8.4.1 General

The method is intended mainly for use with less volatile solvents. If it is used for volatile solvents, there is a risk of errors being introduced in the results due to loss of solvent during the procedure.

If a large number of samples are to be analysed, consideration should be given, even with less volatile solvents, to using the gravimetric method owing to the fact that it enables test portions to be handled faster in parallel. Alternatively, the photometric procedure can be carried out faster by using the same solvent not only to prepare the calibration solution but also for all the other samples. It is not necessary to prepare as many calibration solutions. The presence of small amounts of solvent in the test solution is not relevant at the high dilution used.

Before using the photometric method, it is necessary to verify the suitability of the method for the sample/solvent combination to be used. If this validation is successful, it is not necessary to repeat the verification for subsequent samples of the same kind.

Depending on the particular measurement, metering and dilution equipment used, it is possible to automate the procedure significantly.

The test solution shall follow the Beer-Lambert law and shall be stable enough to allow repeatable measurements. If the maximum of the absorption peak is not stable during several repeated measurements, another, more stable, peak shall be selected for the calculation or an assessment of the whole spectrum shall be considered.

8.4.2 Preparation of calibration solution

The calibration solution shall follow the Beer-Lambert law. If a 2 cm spectrophotometer cell is used, a concentration of about 0,15 g/l for yellow dyestuffs (low absorption) and about 0,02 g/l for blue dyestuffs (high absorption) is normally suitable.

Weigh exactly 100,0 mg of dyestuff into a weighing bottle (6.2) and transfer it to a 100 ml volumetric flask (6.5), taking care that none is lost. Add 60 ml of solvent and dissolve the dyestuff in an ultrasonic bath (6.12).

Cool down, if necessary, to room temperature, make up to the mark with solvent and shake well.

The dyestuff concentration in the solution thus prepared is exactly 1,0 g/l and it now has to be diluted so that it follows the Beer-Lambert law (e.g. to 0,2 g/l or 0,02 g/l).

NOTE If a volatile solvent is being used, accurate dilution may be difficult and consideration should be given to using the gravimetric procedure (see 8.3).

Owing to the low concentration of dyestuff in the solution, the density of the solution to be diluted is nearly identical to that of the pure solvent, so the mass of solution required for the dilution can be obtained using Equation (2):

$$m = V \cdot \rho \tag{2}$$

where

m is the mass, in grams, of solution required;

V is the volume, in millilitres, of solution required;

ρ is the density, in grams per millilitre, of the solvent at 23 °C.

Weigh the required mass of solution into a weighing bottle or in a syringe (for volatile solvents) and transfer to a 100 ml volumetric flask (6.5). Rinse the weighing bottle or syringe with solvent, adding the rinsings to the solution in the flask, make up to the mark with solvent and shake well.

8.4.3 Preparation and dilution of test solutions

Prepare test solutions as specified in 8.2. Dilute each to a concentration comparable to that of the calibration solution.

For example, to obtain a concentration of 0,02 g/l, two dilution steps are required:

a) 1 g/l;

b) 0,02 g/l.

These steps are carried out in the same way as for the preparation of the calibration solution. It is important that the amount of sample weighed out is not too low, to reduce errors due to loss of solvent. The amount weighed out shall therefore be over 1 g. The use of a 10 mm cell can reduce the number of dilution steps necessary.

EXAMPLE Consider a dyestuff which has an estimated solubility of about 100 g/l in cyclohexanone.

The test solution of the dyestuff in cyclohexanone will therefore contain 2 g of dyestuff and 20 ml of solvent. As the density of cyclohexanone is 0,95 g/ml, the mass of the solvent will be 20 ml × 0,95 g/ml, i.e. 19 g. The total mass will therefore be 2 g + 19 g, i.e. 21 g.

For the dilution, 0,1 g of dyestuff is needed, i.e. one-twentieth of the total mass.

Assuming that all the dyestuff is dissolved, 21/20 g, i.e. 1,05 g, of the supernatant liquid is needed.

Weigh this amount of supernatant liquid into a weighing bottle and transfer to a 100 ml volumetric flask. Rinse the weighing bottle with solvent, adding the rinsings to the solution in the flask, make up to the mark with solvent and shake well.

The solution thus obtained has a concentration of 1 g of dyestuff per litre.

The dilution to the final concentration of 0,02 g/l is carried out in the same way, i.e. by diluting the equivalent mass of the 1 g/l solution in another 100 ml flask.

8.4.4 Procedure

8.4.4.1 Zeroing

Before making measurements on a series of test solutions, zero the spectrophotometer (6.11) by measuring the spectrum of the pure solvent for use as a reference baseline, thus avoiding any solvent-related effects on the spectra obtained.

8.4.4.2 Calibration

Carry out a calibration run with the calibration solution (see 8.4.2), measuring the absorbance of the calibration solution at the same wavelength or over the same range of wavelengths as will be used with the test solutions (see 8.4.4.3).

8.4.4.3 Measurements

Use one of the following procedures:

- with solutions which give a stable peak maximum, measure the absorbance at the peak maximum;
- with solutions which do not give a stable peak maximum at the peak of interest, measure the absorbance of another, more stable, peak;
- measure the whole spectrum and determine the area under a defined part of the curve.

Shake the solutions well before making any measurements. Rinse the spectrophotometer cell three times with the test solution between measurements or use disposable cells.

8.4.5 Expression of results

Calculate the relative amount of dyestuff in the test solution using Equation (3):

$$D = \frac{A_\mathrm{s} \cdot c_\mathrm{c}}{A_\mathrm{c} \cdot c_\mathrm{s}} \tag{3}$$

where

D is the relative amount of dyestuff in the test solution;

A_s is the absorbance of the diluted test solution (see 8.4.3) at the peak maximum chosen;

c_c is the concentration of the dyestuff in the calibration solution, in grams per litre;

A_c is the absorbance of the calibration solution at the peak maximum chosen;

c_s is the final concentration of the supernatant liquid in the diluted test solution (see 8.4.3), in grams per litre.

Using Equation (4), calculate the ratio between the amount of dyestuff and the volume of solvent in the supernatant solution to determine the concentration of the dyestuff in the solvent, which corresponds to the solubility, S, under the conditions used (see 3.1):

$$S = \frac{c_\mathrm{s} \cdot D \cdot \rho}{c_\mathrm{s} \cdot (1 - D)} = \frac{D \cdot \rho}{1 - D} \tag{4}$$

where

S is the solubility of the dyestuff, in grams per litre;

ρ is the density of the solvent, in grams per litre.

9 Test report

The test report shall contain at least the following information:

a) all details necessary for the identification of the product tested, together with its non-volatile-matter content;

b) a reference to this International Standard (ISO 7579);

c) the solvent used and its degree of purity;

d) the method of mixing the dyestuff and the solvent;

e) the method used to determine the amount of dissolved dyestuff (gravimetric or photometric);

f) the result of the test, expressed as indicated in 8.3.4 or 8.4.5;

g) any deviation from the procedure specified;

h) the date(s) of the test.

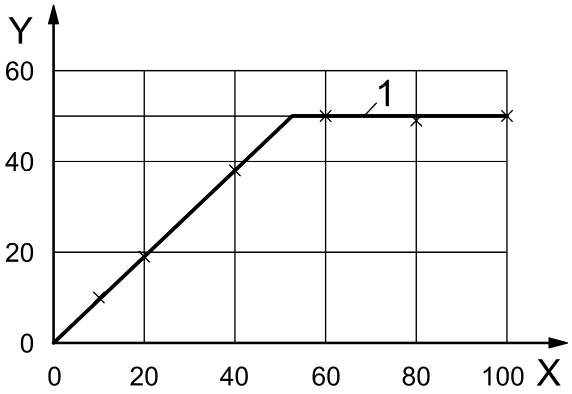
Annex A
(normative)

Solubility calculations

A.1 Dyestuff with a definite saturation concentration

For a dyestuff which gives a definite saturation concentration in the chosen solvent, the solubility has been reached when an increase in the mass of the test portion results in no further increase in dissolved matter. The solubility may be determined by simply inspecting the results (see Table A.1) or by plotting a graph (see Figure A.1).

If the saturation concentration corresponds to less than 90 % of the mass of the test portion added to 1 l of solvent, both values shall be recorded: for example, a saturation concentration of 170 g/l with a test portion of 200 g/l. Such cases may occur with dyestuffs containing insoluble impurities, for example salts.



Key

X mass of test portion, in grams

Y solubility, in grams per litre

1 saturation concentration (= solubility)

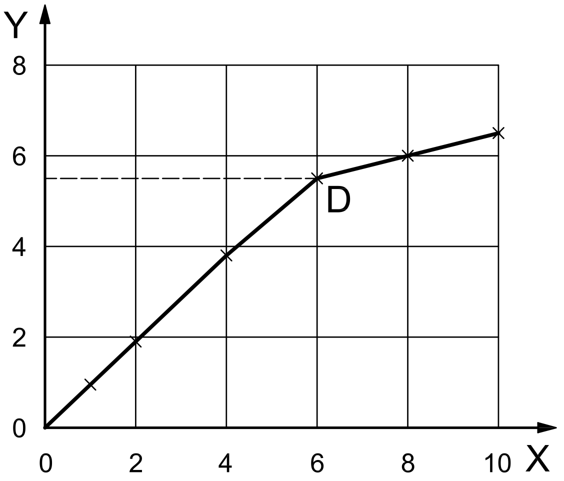
Figure A.1 — Solubility of a dyestuff which gives a definite saturation concentration (graphical presentation of results)

Table A.1 — Solubility of a dyestuff which gives a definite saturation concentration (tabular presentation of results)

Mass of test portion added to 1 l of solvent g	Mass of dyestuff dissolved in 1 l of solvent g	Proportion of test portion dissolved in solvent %
10	10	100
20	19	95
40	38	95
60	50	83
80	49	61
100	50	50

A.2 Dyestuff with an "indefinite" saturation concentration

When the results are treated graphically, a dyestuff with an indefinite saturation concentration shows, above a certain point, a distinctly lower rate of increase in the proportion of the test portion dissolved with increasing mass of test portion (see Figure A.2). The solubility limit is determined graphically as the concentration at the discontinuity D, provided that the discontinuity represents a concentration at which at least 90 % of the added dyestuff is dissolved. If this is not the case, determine the solubility limit as outlined in Clause A.3.



Key

X mass of test portion, in grams

Y concentration of dyestuff, in grams per litre

D solubility limit

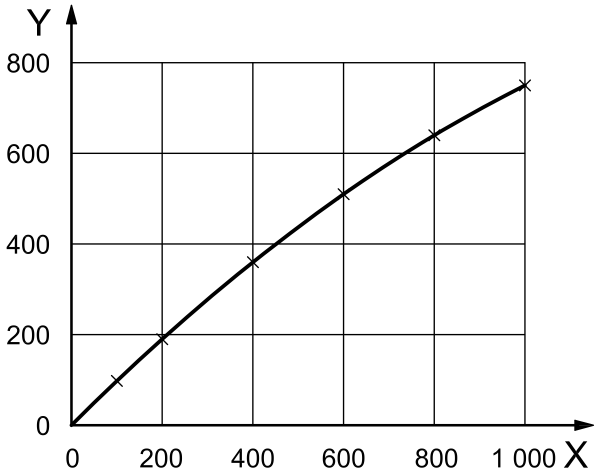
Figure A.2 — Solubility of a dyestuff which gives an "indefinite" saturation concentration (graphical presentation of results)

Table A.2 — Solubility of a dyestuff which gives an "indefinite" saturation concentration (tabular presentation of results)

Mass of test portion added to 1 l of solvent g	Mass of dyestuff dissolved in 1 l of solvent g	Proportion of test portion dissolved in solvent %
1	0,95	95
2	1,9	95
4	3,8	95
6	5,5	92
8	6,0	75
10	6,5	65

A.3 Dyestuff with no saturation concentration

With some combinations of dyestuff and solvent, it is not possible to determine the solubility because the proportion of dyestuff dissolved is dependent on the mass of the test portion and no clear discontinuity is observed (see Figure A.3). In most cases, the solubility increases steadily but not in direct proportion to the mass of the test portion. In such cases, the solubility results shall be presented either graphically (see Figure A.3) or in tabular form (see Table A.3).



Key

X mass of test portion, in grams

Y concentration of dyestuff, in grams per litre

Figure A.3 — Solubility of a dyestuff which gives no saturation concentration (graphical presentation of results)

Table A.3 — Solubility of a dyestuff which gives no saturation concentration (tabular presentation of results)

Mass of test portion added to 1 l of solvent g	Mass of dyestuff dissolved in 1 l of solvent g	Proportion of test portion dissolved in solvent %
100	98	98
200	190	95
400	360	90
600	510	85
800	640	80
1 000	750	75

A.4 Indication of effect of viscosity

If the solubility limit cannot be determined because of a large increase in viscosity with increasing mass of test portion, the last value obtained shall be stated, together with an appropriate note.

EXAMPLE 850 g/l — a solubility limit was not reached because of a large increase in viscosity.

If the last value obtained corresponds to more than 90 % of the mass of the test portion, the solubility shall be stated with the addition of “greater than”, for example > 850 g/l.

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